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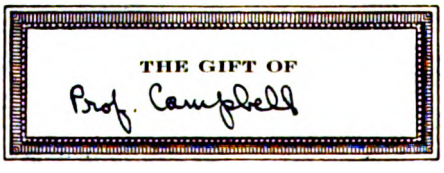

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Transactions
OF
The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. XVI. SEPTEMBER, 1920. PART 1.

SYMPOSIUM AND GENERAL DISCUSSION ON THE MICROSCOPE: ITS DESIGN, CONSTRUCTION AND APPLICATIONS.

THE FARADAY SOCIETY, the ROYAL MICROSCOPICAL SOCIETY, the OPTICAL SOCIETY, and the PHOTOMICROGRAPHIC SOCIETY in co-operation with the Technical Optics Committee of the BRITISH SCIENCE GUILD, meeting in joint session, held a Symposium and General Discussion on "THE MICROSCOPE: ITS DESIGN, CONSTRUCTION AND APPLICATIONS," on Wednesday, January 14th, 1920, in the Rooms of the Royal Society at Burlington House, Piccadilly, London, by kind permission of the President and Council.

The purpose of the Symposium and Discussion, which was organised by a Joint Committee of the Co-operating Societies, at the initiative of Sir Robert Hadfield, Bart., was:—

(1) To stimulate the study of and research in microscopical science in the United Kingdom by indicating lines of progress in the mechanical and optical design of the instrument, showing by means of exhibits recent improvements in the

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microscope and its technique and the varied uses to which the microscope can be applied as an instrument of research in the sciences, arts and industries.

(2) To encourage the manufacture in this country of the highest class of instrument and of the optical glass required for that purpose.

The meeting extended over two sessions: from 4.15 to 6.30 and from 8.15 to 10.30 p.m. The exhibition, which was probably the most important of its kind ever held in this country, took place during the afternoon preceding the meeting, in the Library of the Royal Society. The list of exhibits is printed as an Appendix to this Report.

The total attendance at the exhibition and meeting was not far short of one thousand, and the proceedings throughout were of an enthusiastic nature.

The meeting was presided over by **Sir Robert Hadfield, Bart., D.Sc., D.Met., F.R.S.,** President of *The Faraday Society,* supported by **Mr. J. E. Barnard,** President of the *Royal Microscopical Society,* **Professor F. J. Cheshire, C.B.E.,** President of the *Optical Society,* **Mr. F. Martin Duncan,** President of the *Photomicrographic Society,* and **Dr. R. Mullineux Walmsley,** Chairman of the *Technical Optics Committee of the British Science Guild.*

The CHAIRMAN, **Sir Robert Hadfield,** opened the proceedings with the following remarks:—

Whilst we must not congratulate ourselves too soon, we can at any rate say, by the large numbers present, by the extraordinary variety and number of valuable papers submitted, by the exhibits, both historical and modern, also by the interest shown generally, that this Symposium is going to aid in throwing more light on the important subjects with which it is attempting to deal.

I earnestly hope, as I am sure we all do, that as a result of our proceedings, not only will our knowledge—and knowledge is power—be increased, but that this country will be rendered independent of foreign supplies in products which it is so vital should be made at home. In this respect I should like to read a valuable letter I have received from that public-spirited and broad-minded citizen Lord Burnham, who is taking great interest in our deliberations and who had hoped to be present. In his letter he is kind enough to say:—

"It is, as you say, of vast importance to our future that we should do all we can to assist the British optical industry to meet foreign competition and to strike out new lines of advance for itself. We all know how far we were left behind in the days before the war and this time it is up to us to make good once for all.

I wish I could come myself, but I am deeply engaged on that day. It is a great thing that you and your colleagues should put yourselves at the head of such a movement."

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I think we all feel stimulated by such encouraging words from a man like Lord Burnham, who, while not a scientist or technician, sees the great importance of this movement.

It is also a great satisfaction to find so many well-known representatives of science and technology taking part in our Symposium to-day. America has contributed several valuable communications, including those of Prof. Sauveur, who has done so much for the microscope and metallography, Dr. Zay Jeffries, who has made the subject of grain size peculiarly his own, and others.

We have important communications from France and Italy in the papers of Monsieur Eugene Schneider, Prof. H. le Chatelier, Signor Giolitti, and others.

As regards our own country, I venture to say that the host of Addresses and Papers, some forty in all, are unique, and of a most valuable nature. The Addresses include those to be presented by Sir Herbert Jackson, Mr. Barnard, Prof. Cheshire, and Prof. Conrady, each of them meriting commendation of the highest kind. As regards the authors of the large number of papers presented, it is not possible to mention here the names, for they are so numerous, but it can be added that the general standard of the papers is exceedingly high, and we thank those many contributors most heartily for the trouble and pains they have taken in preparing their communications.

May I say, too, on your behalf, how extremely grateful we are to the authors of the Addresses and Papers, also to the Exhibitors and the many others who have worked with such energy to make the Symposium not merely, I trust, a success, but one from which will spring benefits, both scientific and practical, of the highest order.

I wish to add one word with regard to the most valuable historical collection submitted by the Education Department. I refer to that from the Science Museum, South Kensington. I also take this opportunity of offering our heartiest congratulations to Sir Francis Ogilvie, the Director of that Museum, upon his recent well-deserved Knighthood.

We have, too, with us this evening many important Members and visitors who have done much for the microscope. Amongst them is my friend Dr. J. E. Stead, who has greatly helped metallography. I am sure you will all be glad to learn that he is in May next to become President of that important body, the *Iron and Steel Institute*. We wish him health and strength and a most successful term of office.

I am sure I shall be excused for referring to family matters. Of course, as family matters are, it is strictly private, but as we are one big family to-night we should like you all to share in our joys. It is not often that after quite a considerable interval of time it is possible to bring together the Founders of a Society. The changes and chances of this mortal life step in and sadly break continuity, but in this special case I am glad to tell you we have present with us this evening, with one unavoidable exception—and, happily, this is not owing to the member in question not being in the land of the living—all the Founders of the Faraday Society. I refer to Mr. Sherard Cowper-Coles, Mr. W. R. Cooper, Prof. F. G. Donnan, Dr. F. M. Perkin, Mr. Alexander Siemens, Mr. James Swinburne

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and Mr. F. S. Spiers. It must be a great satisfaction to them to see this magnificent meeting, as one of the fruits of their labours in the past; that is, in seeing the Society they founded, aided by the sister Societies, in the earnest set purpose of assisting our Empire in this important question of improving our resources in optical matters. All honour to the men mentioned, and I am sure that I shall be voicing your feelings in offering them our heartiest congratulations.

Whilst this is a meeting of the "Micro-Intellectuals," may I now descend to earth and remind you that our full programme has its drawbacks. We have the time limit to consider, and I beg that this be borne in mind. If I have occasionally to use the closure it will not be because the words being uttered are not considered words of wisdom, but that the evening is not long enough. I will now try to set the example by making my own remarks as brief as possible.

Sir Robert Hadfield then presented the following "Introductory Address," to the salient features of which he briefly drew attention.

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INTRODUCTORY ADDRESS

By SIR ROBERT HADFIELD, Bart., D.Sc., D.Met., F.R.S.,

President of the Faraday Society.

SECTION I.—INTRODUCTION.

As the result of some suggestions I made several months ago to the Council of the Faraday Society, it was arranged to hold this present Symposium on "The Microscope and its Applications." The Royal Microscopical Society (Mr. J. W. Barnard, President); the Optical Society (Professor F. J. Cheshire, President); and the Photomicrographic Society (Mr. F. Martin Duncan, President) all most cordially approved and agreed to co-operate with us. In view of the fact that the objects of the Faraday Society, as set forth in its Constitution, are not only to promote the study of Electrochemistry, Electrometallurgy, Physical Chemistry and Kindred Subjects, but also Metallography this Symposium is specially appropriate. It is only, or at any rate chiefly, the last named Branch of Research—Metallography—my own remarks are meant to cover, that is, I do not pretend in this Address to deal with the Work of the Microscope as employed by the Geologist, the Zoologist, the Biologist, and other Branches.

During the preparation of this Address I found the interesting frontispiece of the Book by George Adams, "ESSAYS ON THE MICROSCOPE." This was published July 1st, 1787, and contains a Practical Description of the Most Improved Microscopes, revised by Frederick Kanmacher, F.L.S., 1798. I thought this illustration particularly appropriate to form the frontispiece to this present Address of mine. The quaint wording at the foot of the Engraving

"Truth discovering to Time, Science instructing her Children in the Improvements on the Microscope,"

well describes the object of our present Symposium.

As regards the modern application of the Microscope including that to Metallography, below is a portion of the preface to Monsieur Félix Robin's Work "Treatise on Metallography," contributed by Professor F. Osmond, who did so much for Metallurgy, and from

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whose work we are to-day greatly benefiting. Robin has, alas, himself passed away during the Great War, gloriously devoting his life on the Field of Battle on behalf of his Country. I make no apologies for referring to this tribute to the Metallographist and for quoting in full the wise words of Osmond. These are well worthy of consideration to-day, and the reasons given by him will, I trust, cheer many an author and many a worker in the fields of research.

Osmond said: "To write a treatise on a branch of Science in process of active development is an arduous task, especially when the author is not a professor and the book not the natural synthesis of the course. It is also a thankless task, for the work of to-morrow will amplify and correct that of to-day. In a few years' time, too, the old edifice must be rebuilt because the new generation no longer deems it sufficiently comfortable in its old form. We ought, therefore, to be indebted to those who have the courage—which I have always lacked—to collect and collate scattered material. Those who continue the work are thereby saved the trouble of lengthy visits to libraries and the search for documents of sometimes questionable value disseminated in the periodicals of all civilised countries. But M. Robin's book is not a mere compilation. The author, whose numerous papers have evoked the attention of, and have been the subject of numerous awards by, the British Iron and Steel Institute and others, has been working whole-heartedly for some years past in the direction of extending our knowledge of Metallography and its kindred Sciences. His contributions to this Science have been most useful, and he is thus in a position to enrich the present treatise by his personal experience and minute observations, to the great benefit of those who will follow him."

> "*La science est un pays plein de terres désertes;*
> "*Tous les jours nos auteurs y font des découvertes.*
> "*Mais ce champ ne se peut tellement moissonner,*
> "*Que les derniers venus n'y trouvent à glaner.*"

Work of the Various Societies taking part in this Symposium.

The Faraday Society.—Turning to the work of each of the Societies taking part in this Symposium, I deal with that of the Faraday Society in a separate paper presented to this Symposium, entitled "The Work of the Faraday Society and a brief Reference to Michael Faraday." I will therefore not add anything further here. (*See Appendix II, p. 251*).

Royal Microscopical Society.—The Royal Microscopical Society was established in 1839. The late Dr. H. C. Sorby, F.R.S., of Sheffield, the Founder of Modern Metallography and of whom a portrait is given in Fig. 1, was President of this Society in 1876 and 1877. The famous Microscopist, Dr. W. Dallinger, F.R.S., of whom a portrait is given in Fig. 2, and who lived in Sheffield for a number of years, was also President, in the years 1884-7.

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Amongst other Past Presidents of this important Society have been Sir Richard Owen, 1840; Edwin Lankester, 1858; John Thomas Quekett, 1860; Lord Avebury, 1907; Sir Edwin Ray Lankester, 1909; Prof. H. G. Plimmer, 1911; and to-day Mr. J. E. Barnard.

It was in November, 1866, that Mr. Secretary Walpole notified the President that Her Majesty had been graciously pleased "to command that the Society shall be styled the Royal Microscopical Society."

Singular to say, notwithstanding his early work in 1857-1863, Dr. Sorby, even in his own Presidential Addresses in 1876-1877 to the Royal Microscopical Society, made no reference to the use of the Microscope for Metallurgical Research. Apparently, he himself had not then applied his method of study, but the germ was there waiting to be developed. Professor W. G. Fearnsides has pointed out in his interesting account of Sorby's lifework in the first Sorby Lecture delivered before the Sheffield Society of Engineers and Metallurgists in 1914, "On some Structural Analogies between Igneous Rocks and Metals," that it was in the year 1885, by the use of Lenses of high resolving power and comparatively large magnification, Sorby first saw the true composite nature of the "pearly constituent" of Steel as an aggregate of parallel plates. This discovery was the earliest recognition of the formation of crystals from a solid solution, and may be regarded as the crowning achievement of his microscopical research. He announced this discovery to the Iron and Steel Institute in 1886, and in 1887 presented to the same Institution his historical Paper on "The Microscopical Structure of Iron and Steel," which gave a full account of his methods and the results he had obtained.

A well-known American writer, in a biographical sketch of Sorby published in "The Metallographist" for April, 1900, stated: "Whatever has been accomplished since in Microscopic Metallography has been done by following in his footsteps. To Dr. Sorby, and to him alone, is due the pioneer's honour."

I had at first intended to include in this Address my remarks regarding the great work performed by Sorby for "The Metallographist." In view, however, of the importance of the subject, and that some of our younger members may not be aware of the facts, I have thought it best to embody and present these in a separate short communication entitled "The Great Work of Sorby."

Optical Society.—As regards the Optical Society, which now has its Headquarters at the Imperial College of Science and Technology at South Kensington, this was founded in 1899, its first President being Mr. W. H. E. Thornthwaite, F.R.A.S. Subsequent Presidents have been Dr. R. M. Walmsley, Professor Silvanus Thompson, Dr. W. Rosenhain, Sir Richard Glazebrook, Sir David Gill, and to-day Professor Cheshire, C.B.E., who did such excellent work in the War.

Photomicrographic Society.—The Photomicrographic Society was founded in 1911 by a small band of Microscopists and Photographers, including Fellows of both the Royal Microscopical and Photographic Societies, having for its objects, to quote from its Rules, "the study

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of Photomicrography and the discussion and demonstration of any subjects of interest concerning it." From the first the Society was a success, as evidenced by continual increase of Membership, and this is perhaps due to the wide field in Research, Engineering, Natural History, Industrial and other Processes, in which the Microscope is essential. This is also shown in the diverse nature of the subjects in which individual members are specially interested, but who alike have to record their observations by Photography. Others again are interested purely in the optical equipment of the Microscope and the special problems presented to the photomicrographic worker. The essential importance of correct microscopic technique, especially proper illumination to obtain a correct image, has always been recognised, and great attention has been paid to the mechanical side, as shown by apparatus designed and built by several members and exhibited from time to time.

Mr. F. Martin Duncan now occupies the Presidential Chair, and Mr. J. E. Barnard was President in 1915-16. A Medal is awarded annually, for the best results in Photomicrography from both the microscopical and photographic point of view.

The Society meets twice monthly at King's College, and has papers on the many subjects in which the use of the Microscope is essential, together with other meetings of a less formal character for discussion, exhibition of photomicrographs, and apparatus connected with Photomicrography.

For the foregoing information I am indebted to the Honorary Secretary and Treasurer, Mr. J. G. Bradbury, who has done so much good work on behalf of this useful Society.

British Science Guild.—The Committee on the Microscope appointed by this Body, with its Chairman, Dr. Walmsley, have also been kind enough to give much useful help with regard to our Symposium.

It will be seen therefore that the Faraday Society has been successful in enlisting the co-operation and aid of the various special Societies who are also immediately interested in improving Research Work in Microscopy.

OBJECTS OF THE SYMPOSIUM.—The objects of the Symposium are :—

(*a*) Improvement in the technique of the Microscope itself, including its manufacture.

(*b*) Improvement in Lenses including Eye-pieces and Objectives of High Power.

(*c*) Improved application of the Microscope for Research in Ferrous and Non-Ferrous Metallurgy.

With these objects all will be in agreement, and if as a result of this Symposium they are successfully carried out and attained, as I am confident will be the case, our gathering will be not only

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noteworthy, but will prove to be of great service to those interested, in our own Country, America, and elsewhere.

PRESENT AND FUTURE WORK.—As regards the particular direction in which Metallurgists should look in the future for further help from the Microscope, may I suggest that one of the objects we ought to have in view should be to obtain increased knowledge from examinations at higher magnifications, that is to say, 5,000, 8,000 and still higher. This may seem ambitious, and I may be wrong as to the value of the knowledge to be so obtained, but I hope not. If there is anything in my belief, a wide vista opens out for further Research Work.

I am contributing along with Mr. T. G. Elliot, F.I.C., a special paper on this important aspect of the subject, entitled " Photomicrographs of Steel and Iron at High Magnification," which I hope will be of interest to our members.

In the past both in England and in America there has been far too much dependence on Germany and Austria for the supply of the best type of Microscope, including constructional details, and high-quality Objectives and Eye-pieces. It is most desirable that in future this situation should be avoided. Forewarned is forearmed, and every possible means must be taken in a fair and open manner to remedy this situation by private enterprise and research, and if necessary by Research Associations aided by the grants allocated by Parliament for such purposes.

To show that it is of the highest importance that this Country should be independent of foreign aid in its supplies of this nature, it may be added that had it not been for the enterprise of just one British Firm with regard to the supply of Optical Glasses at the outbreak of War, we might have been absolutely stranded in the supply of the necessary products, both for apparatus and glassware, so essential in sighting and other instruments of observation used in Modern Warfare.

By these remarks I do not wish to disparage the work of those who until recently have been Enemies, and who in the past wisely equipped themselves by means of Apparatus and Appliances of all kinds as well as by encouraging scientific development. Good work proceeding from any nationality stands fast for all time. Let us, however, now learn the lesson and benefit from the experience gained by us during the War at such bitter cost. It has to be admitted that our Instrument Makers were then necessarily largely employed in other directions and were unable to cater for the requirements of the Microscopist. They could not therefore devote the time so essential for improving not only the mechanical but the optical details of the Microscope, including its Objectives and Eye-pieces. Notwithstanding the many advances made during the War by the Chemist, the Electrician, the Metallurgist, the Engineer, and others, no special claim can be made that much progress has been made by the Microscopist. As far as can be gathered, the methods and appliances now used do not show great advance on those prior to the War. In saying

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that it is not meant to indicate that knowledge has not been accumulated and that, for example, we shall in the future be dependent upon foreign supplies as in the past; it is hoped quite the contrary. It is one of the main objects of this Symposium to bring forth and prove that all these requirements can and will be met by the Anglo-Saxon, or at any rate that this will be possible in the immediate future.

It should be added that there stands out very prominently in this connection the important work done on behalf of Glass Technology by Sir Herbert Jackson, K.B.E., to whom we are greatly indebted, and who will give us an important Address this evening.

Reference should also be made to the excellent work carried out on this subject by the National Physical Laboratory, where systematic work on the attack of various refractory bodies by molten glass under carefully standardised conditions has been continued, together with work on the production of crucibles increasingly resistant to such attack. Progress has been made in the application of fused zirconia as a lining for crucibles. In the course of this work special phenomena have been observed in the attack which occurs in some cases at the bottom of the crucible, and in others, at the level of the surface of the glass. These phenomena have been studied by means of experiments on the mode of solution of such substance as wax, naphthaline and plaster-of-paris in ordinary solvents at room temperature where the phenomena could be observed. Most of the features met with in the attack of molten glass on crucibles have been reproduced in such experiments, and a method of preventing the worst features of such attack has been tried and found successful in the model experiments. In addition reference should be made to the valuable work done by the Society of Glass Technology at the University of Sheffield, in which Dr. W. E. S. Turner, the honorary secretary, has played so important a part.

It is certainly most necessary that we should not be behind but abreast of our Foreign competitors in the making of Microscopes and Lenses or their use. One of the prominent objects in holding the Symposium is to arouse still more interest in the advancement of this work.

SECTION II.—HISTORY OF THE MICROSCOPE.

Ancient Times to 1600 A.D.

If the Microscope is considered as an Instrument consisting of one Lens only, it is not at all improbable that it was known to the Ancients, and even to the Greeks and Romans. The minuteness of some of the pieces of workmanship of the Ancients would appear to indicate that they must have been executed by the use of Magnifying Glasses. Many passages in the Works of Pliny, Plutarch, Seneca, and others clearly indicate this.

There is reason to believe that the magnifying power of transparent media with convex surfaces was known very early. The convex Lens of rock crystal was found by Layard among the ruins of the Palace of Nimrod. Seneca describes hollow spheres of glass filled with water as being mainly used as magnifiers. It is practically certain that

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the perfect gem cutting of the Ancients could not have been attained without the use of magnifiers.

In the Book "Essays on the Microscope" by George Adams, Mathematical Instrument Maker to His Majesty (1787), being "A Practical Description of the Most Improved Microscopes," which was one of the Standard Works at that time, Adams said: "It is generally supposed that Microscopes were invented about the year 1580, a period fruitful in discoveries. The honour of the Invention is claimed by the Italians and the Dutch; the name of the Inventor appears, however, lost."

With regard to the many interesting facts relating to the early History of the Microscope, two valuable contributions have been made by Dr. Charles Singer, M.D., "Notes on the Early History of the Microscope" read before the Royal Society of Medicine in 1914, and "The Dawn of Microscopical Discovery," before the Royal Microscopical Society in 1915.

In giving the following information I have taken the liberty of freely making use of the valuable Researches of Dr. Singer, who points out that there have been three main epochs in the History of Microscopical Discovery. There was the Pioneer Period, extending to about 1660, the Classical Period, covering half-a-century or more from about 1660, and including the work of the great Microscopists, Hooke, Grew, Malpighi, Leeuwenhoek and Swammerdam, and finally the Modern Period, dating from the Optical Discoveries of Newton.

The earliest microscopical observation known is stated by Dr. Singer to be of Seneca (circa A.D. 63) who in his "Quæstiones Naturales" said that "Letters, however small and dim, are comparatively large and distinct when seen through a glass globe filled with water."

The properties of curved reflecting surfaces, and even to some extent of Lenses, were known to the ancients, and to some mediæval writers, such as Roger Bacon. The invention of convex spectacles is attributed to Salvino d'Amarto degli Armata, of Florence, and to Alessandro de Spina, of Pisa, about the year 1300, and these aids to vision were familiar to many throughout the fourteenth, fifteenth and sixteenth centuries. During this period the optical properties of Lenses were investigated by the penetrating genius of Leonardo da Vinci (1452–1519) and by the mathematical skill of Maurolico (1494–1575), while convex spectacles must have been on the nose of many a careful illuminator of manuscripts.

Up to this time Dr. Singer points out there is no single instance on record of these glasses having been used for the investigation of nature and that even the many illuminated manuscripts of the fifteenth and sixteenth centuries, especially of the Flemish school, do not suggest the use of magnifying glasses.

The first illustrated publication, for which there is evidence of the use of a magnifying glass, appeared in the year 1592 at Frankfort, bearing the name of George Hœfnagel (1545–1600). The volume consisted of a series of plates engraved on copper, illustrating common objects of nature, but drawn with exceptional skill and minute accuracy. Some few of these drawings revealed enlarged details which would

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have been hardly distinguishable to the unaided eye. These remarkable figures are stated to have been the work of Hœfnagel's son, Jacob (1575).

It must be remembered, however, that the occasional use by a naturalist of a simple Lens of low magnifying power could have but little influence on the advance of knowledge. It was not until the Classical Period with the invention of Lenses of very short focus that the simple Microscope became a valuable means of Research. In the Pioneer Period it was rather the discovery that Lenses could be combined into the Telescope and the Microscope that gave the first stimulus to investigation. These compound instruments were invented about the year 1610.

1600 TO 1700 A.D.

The Dutchman Zacharias, miscalled Jansen, and his son made Microscopes before the year 1619. It was he who, whilst still a lad, had worked with his father, who was a spectacle maker, and appears to have discovered accidentally the principle of a Telescope by placing two Lenses together in a tube. The invention of the Microscope followed about that time, though the exact date is unknown. In the year 1619, Cornelius Drebbel, of Alkomar, brought a Microscope which was made by the Jansens with him into England and showed it to William Boreel, who was Dutch Ambassador to France, and eventually to England. It is, however, added that Drebbel's instrument was not strictly what is now meant by the Microscope, but was rather a kind of Microscope–Telescope, somewhat similar in principle to certain apparatus described by Mr. Aepinus in a letter to the Academy of Sciences, St. Petersburg. This was formed of a copper tube six feet in length and one inch in diameter. On the other hand, Dr. C. Singer, in his interesting Paper on "The Historical Aspect of the Microscope," does not think this was the case.

A portrait of Jansen is given in Fig. 3. A photograph is also given of Hans Lipperhey (Fig. 4), who is described as the inventor of the second Microscope, Jansen being referred to as the inventor of the first one, that is of the special type described probably in the beginning of the Seventeenth Century.

Dr. Hooke, the author of the famous "Micrographia" in 1665, described means of utilising small drops or globules of glass in a Microscope, and said that by means of this he had been able to distinguish the particles of bodies not only a million times smaller than the visible points, but even to make these visible whereof millions of millions would hardly make up the bulk of the smallest visible grain of sand; so prodigiously do these exceedingly small globules enlarge our prospect into the more hidden recesses of Nature. Di Torre of Naples also largely made use of these globules for his well-known investigations.

As regards Hooke's Book referred to, it may be interesting to give a facsimile (Fig. 5) of the title page as it appeared in 1665. Hooke was a Fellow of the Royal Society, and a facsimile of his signature as it appears in the famous "Roll Call of Fellows" is given at the foot of the front page, in Fig. 5.

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As an interesting example of the examination done by Hooke in 1664, and simple as this may seem now, I give in Fig. 6 the result of an investigation he carried out on the point of a small needle, which to use his own words, was

made ſo ſharp that the naked Eye is unable to diſtinguiſh any of its Parts. This, notwithſtanding, appeared before his Microſcope as in the Figure at *a a*, where the very Top of the Needle is ſhewn above a Quarter of an Inch broad; not round or flat, but irregular and uneven.

The whole Piece we have here the Picture of, (according to the Scale given with it) is little more than the twentieth Part of an Inch in Length, and appeared to the naked Eye exquiſitely ſmooth and poliſhed; but, as ſeen by the Microſcope, what a Multitude of Holes and Scratches are diſcovered to us? How uneven and rough the Surface! how void of Beauty! and how plain a Proof of the Deficiency and Bunglingneſs of Art, whoſe Productions when moſt laboured, if examined with Organs more acute than thoſe by which they were framed, loſe all that fancied Perfection our Blindneſs made us think they had! Whereas, in the Works of Nature, the farther, the deeper our Diſcoveries reach, the more ſenſible we become of their Beauties and Excellencies.

But to return to the Object now before us; A, B, C, repreſent large Hollows and Roughneſſes, like thoſe eaten into an Iron-Bar by Ruſt and Length of Time. D is ſome ſmall adventitious Body ſticking thereto by Accident.

b. b. b. ſhew the End where this ſmall Piece of Needle was broken off, in order to take the better View of it.

As ſharp as a Needle is a common Phraſe, whereby we intend to expreſs the moſt exquiſite Degree of Sharpneſs; and, indeed, a Needle has the moſt acute Point Art is capable of making, however rude and clumſy it appears when thus examined. But the Microſcope can afford us numberleſs Inſtances, in the Hairs, Briſtles, and Claws of Inſects; and alſo in the Thorns, Hooks, and Hairs of Vegetables, of viſible Points many Thouſands of times ſharper, with a Form and Poliſh that proclaim the Omnipotence of their Maker.

Another investigation was carried out by Hooke on the "edge of a razor," and to quote his words,

Figure repreſents the Edge (about half a Quarter of an Inch long) of a very ſharp Razor well ſet upon a good Hone, and ſo placed between the Object-Glaſs and the Light, that there appeared a Reflection from the very Edge, which is ſhewn by the white Line *a, b, c, d, e, f.*

When we ſpeak of any thing as extremely keen, we uſually compare it to the Edge of a Razor; but we find, when examined thus, how far from Sharpneſs even a Razor's Edge appears: That it ſeems a rough Surface, of an unequal Breadth from ſide to ſide, but ſcarce any where narrower than the Back of a pretty thick Knife: That it is neither ſmooth, even, nor regular; for it is ſomewhat ſharper than elſewhere at *d*, indented about *b*, broader and thicker about *c*, unequal and rugged about *e*, and moſt even between *a, b*, and *e, f*, though very far in any Place from being really ſtraight.

The Side immediately below the Edge, and what the naked Eye accounts a Part of it, *g, b, y, k*, had nothing of that Poliſh one would imagine Bodies ſo ſmooth as a Hone and Oil ſhould give it; but was full of innumerable Scratches croſſing one another, with Lines here and there, more rugged and deep than the reſt, ſuch as *g, b, y, k, o*, occaſioned probably by ſome ſmall Duſt falling on the Hone, or ſome more flinty Part of the Hone itſelf.

The other Part of the Razor *L L*, which had been poliſhed on a Grind-ſtone, appeared like a plowed Field, full of Ridges and Furrows.

The irregular dark Spot *m, n*, ſeemed to be a little Speck of Ruſt; corroſive Juices generally working in ſuch a manner.

This Examination proves, how rough and unſeemly (had we microſcopic Eyes) thoſe Things would appear, which now the Dulneſs of our Sight makes us think extremely neat and curious: And, indeed, it ſeems impoſſible by Art to give a perfect Smoothneſs to any hard and brittle Body; for *Putty*, or any other ſoft Powder, employed to poliſh ſuch Body, muſt neceſſarily conſiſt of little hard rough Particles, each whereof cutting its Way, muſt conſequently leave ſome kind of Furrow behind it. In ſhort, this Edge of a Razor, had it been really as the Microſcope ſhews it, would ſcarce have ſerved to chop Wood, inſtead of ſhaving a Man's Beard.

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In the Bibliography accompanying the present Address will be found reference to some of the writings of other early workers with the Microscope. For example, Antony van Leeuwenhoek, born at Delft in 1632, constructed the first practical microscope and established the art of properly grinding and polishing the Lenses.

Leeuwenhoek was offered, and accepted, the post of Chamberlain of the Sheriff of the town of Delft, worth £26 annually, and held this for 39 years. In February, 1680, he was made a Fellow of the Royal Society. Although he never came to London, the Diploma of Fellowship was sent to him in a silver box, having the Arms of the Society graven on it. An interesting account of his life is given by the President of the Royal Microscopical Society, Professor H. G. Plimmer, F.R.S., in his Presidential Address in 1913.

Leeuwenhoek did wonderful work with his simple or singular Microscope. The largest magnification he obtained was about 160 in one of his Microscopes: his twenty-six other Microscopes varied from 40 to 133 magnifications. With this simple instrument, as Professor Plimmer points out in his address, Leeuwenhoek discovered a new world, in fact new worlds, for us. He saw for the first time Infusoria, Rotifers, and Bacteria. It is interesting to note in this connection that Charles Darwin took no compound Microscope, but only a simple one, with him on his famous "Beagle" Voyage.

So important was Leeuwenhoek's work that I give a portrait of him (Fig. 8).

In the paper "On the Construction of the Compound Achromatic Microscope" by Charles Brooke, M.A., F.R.S., read before the Royal Institution of Great Britain, March 10th, 1854, he states that the first compound Microscopes on record, such as that of P. Bonnani, about 1697, which was placed horizontally, and that of J. Marshall in the beginning of the eighteenth century, which was vertical, were furnished with central condensers. In later years the development of the illuminating apparatus has by no means kept pace with that of the ocular portion of the Microscope, though scarcely of less importance in attaining the highest perfection in the vision of microscopic objects.

On the authority of Adams, the first three compound Microscopes were said to be those of Hooke, Eustachio Divinis and Philip Bonnani. An account of Divinis' Compound Microscope was read before the Royal Society in 1668 (Philosophical Transactions No. 42).

It must be borne in mind, too, that the progress made in the science of Optics was largely aided by the great work of Sir Isaac Newton, Delavel and Herschel.

1700 TO 1800 A.D.

It is stated by Roberts-Austen also in his "Metallurgy" that the Microscope was first applied to the Examination of Iron and the first records go back to 1722 when Réaumur described the structure of Chilled Castings under the Microscope. François in 1832 took

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the interesting case of the direct reduction of Iron from its Ores, and followed the successive changes by the aid of the Microscope. Roberts-Austen also claims that: "If to these analytical data observations under the Microscope with a magnification of 300 to 400 diameters be added, it is seen that ordinary Iron is merely a metallic network with a close-grained tissue, with submerged scoriaceous opaline, sometimes sub-crystalline, portions, and with little globules and metallic grains ranged in every direction. Sometimes nests of translucent prismatic and bacillary crystals, with metallic portions adhering, are noticed hidden in the paste. These are the grains of Steel which can be made to disappear by heating."

Roberts-Austen thought that Modern Metallography owed some of its development to the use made of it in the Study of Meteoric Irons, also that it is quite possible, as has often happened in the History of Science, that there are several independent origins.

From 1800 A.D. Onwards.

It is interesting to note that in 1808, Widmanstätten oxidized a heated specimen and took polished sections of meteoric iron, thus originating what is now termed "Metallography."

Sorby in 1856 founded Petrography, employing sliced sections in connection with the Microscope for the study of rocks, the structures of which are in some cases analogous to those of metallic alloys. In the year 1864 he made an examination of meteoric iron, also studying various metallurgical products; while in 1885 he discovered Pearlite. When Sorby proposed for the first time to submit a specimen of rail, which had broken and caused an accident, to a microscopic analysis, he was told that it was an insane idea. Sorby's method has since been invaluable for this very purpose—in fact in this Country and in America and elsewhere tens of thousands of photomicrographs have been prepared in connection with the investigation of broken and other rails.

Mr. J. Stuart—himself a veteran of some eighty-four years—of the Clapham Common Optical Works of Messrs. Ross, told me recently that in the 'seventies of the last Century he had repeated visits from Dr. Sorby, who brought various specimens of Steel for examination under the Microscope. Mr. Wenham, Vice-President of the Royal Microscopical Society and the Inventor of the Binocular Microscope, as well as of other microscopical apparatus, was at that time working with Messrs. Ross as their Scientific Adviser. Mr. Wenham was also interested in the study of the structure of steel and had many conversations with the late Dr. Sorby, in fact, constructed for him a high power Binocular which Mr. Stuart believes was the first to be used in connection with the examination of Steel.

Incidentally it may be useful to refer to the fact that the invention of the Oil Immersion Objective was not, as is often imagined, of foreign origin, but was originated by Mr. Wenham in 1870, that is, six or seven

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years before Oil Immersion Objectives were constructed at Jena by Professor Abbe. In a Paper read by Mr. Wenham, entitled "Remarks on High-power Definition," at a meeting of the Royal Microscopical Society in June of that year 1870, he says: "Of course there is no optical advantage attendant upon the use of water in immersion lenses. If a medium of the same refractive power as the glass were to be employed the result would be better. Water, having a low refractive index, an adjustment is required for each thickness of cover, and a difference of adjustment is not so marked and sensitive as in the ordinary dry objective; but if a medium of similar refraction to the glass were to be used, no adjustment would be required for any thickness of cover, supposing the test objects to be mounted thereon (which they generally are), for, in fact, we should then view them all with a front of the same thickness—considering the cover, the front lens and the interposing medium as one."

In addition to reading this Paper, Mr. Wenham exhibited at the same Meeting an Oil Immersion Lens using Cedar Oil and an illuminated object showing great brilliancy. It appears, however, he did not at the time realise that his Oil Immersion could have yielded the great numerical aperture which it afterwards gave in the hands of Professor Abbe.

Another interesting point is the fact that Andrew Ross, the founder of the firm of Messrs. Ross, discovered the system of the Collar Adjustment for Water Immersion Lenses and that Mr. Wenham was the Discoverer of the Oil Immersion which required no Collar Correction.

To show how little was thought of the Microscope as a scientific instrument in connection with the study of Iron and Steel, reference may be made to a Book which I have often found useful, namely, Ferdinand Kohn's "Iron and Steel Manufacture," published about 1868 and based upon a series of valuable articles on "The Manufacture of Iron and Steel," which appeared in "Engineering." In this book Kohn says, in the chapter devoted to "Steel under the Microscope," "An experienced steelmaker can estimate very closely the ferrous quality, chemical composition, tensile and compressive strength of any sample of steel, and even the mode of treatment which it has undergone, by looking at its fracture under the Microscope."

It appears, however, this only meant a small hand Microscope. The following are the words: "A Pocket Microscope of this kind ought to be the companion of every man interested in Steel or Steel Manufacture. Lenses of the usual kind, even if piled up in sets of three or four, are entirely insufficient. The Lens must be of a very small focus, and properly achromatic. A little practice is sufficient to enable the user to "see" through this Lens; but it is, of course, not quite so easy to learn the meaning of what is seen, and to estimate from the appearance the quality of the steel inspected."

Special reference was made to some investigations then being carried out (1868) by Mr. Schott, the Manager of Count Stolberg's Foundry at Islenburg, upon the appearance of liquid and solidifying Cast Iron under the Microscope. Mr. Schott contended that each

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crystal of iron is a double pyramid upon a flat square base, and that the ratio of height to base of the pyramid is proportional to the carbon content. In Cast Irons and hard Steel the crystals approach the cubical form, whilst in Wrought Iron the pyramids are almost flattened down into leaves. In addition the quality of a steel is shown by the arrangement of the crystals. The highest quality of steel has its crystals in parallel positions with their axes in the direction of the pressure exerted on them in working. An examination of the fracture of a good steel in reflected light shows a series of parallel streaks on the surface, whereas in a bad steel several systems of parallel lines can be seen.

The presence of segregated material and size of the grain can also be seen under the Microscope. The absence of the former and the fineness of the latter indicate good material.

The qualities of parallelism of the material and fine grain seem to be due to different causes. The former seems to be caused by the action of heat, and repeated melting is the great panacea in this respect, whilst the latter is brought about largely by working the material; on the other hand working the material seems to prove that parallelism and high temperature bring about the coarsening of grain.

Singular to say, Kohn does not make a single reference to the work of Sorby, which was evidently then only known by few people.

Dr. Dallinger, F.R.S., who resided many years in Sheffield, gave in the Journal of the Royal Microscopical Society, Vol. 17, 1877, page 224, a "Note on the Ultimate Limit of Vision" as applied to modern Microscopical Lenses. He reasoned that mathematicians of the first order, notably Helmholtz, had concluded that the limit of vision had been reached and that the Optician could practically give no further aid. Dr. Dallinger considered that the limit marked out was about the one-hundred-and-eighty-thousandth of an inch, and added that he did not consider the limit of visibility had been reached.

Dr. Sorby in a Paper on the "Limit of the Powers of the Microscope" to the same Society in 1875 referred to an experiment of Dr. Royston-Pigott which showed that the smallest visual angle he could ever distinctly appreciate was a hole 1¼ in. in diameter at a distance of 1,000 yards, which corresponds to about 6 seconds of arc. This visual arc in a Microscope magnifying 1,000 linear would correspond to about three-millionths of an inch.

Tchernoff took up the study of crystallization of Steel, his work being brought before this Country by the late Sir William Anderson. In 1878 Wedding studied Steel by the aid of the Microscope. The work of these investigators caused rapid increase of interest in this subject.

Dr. Martens of Berlin rendered further valuable services, in fact was one of the first to introduce the practical study of Iron and Steel by Metallography. Martens' work commenced about 1878, when he published notes on the Microstructure of Steel.

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In 1880 the use of the Microscope was introduced at Le Creusot Works, and important investigations by Professors F. Osmond and J. Werth were started, and from that date were carried out on the lines first indicated by Dr. Sorby.

In his Book on " How to Work with the Microscope," 1880 edition, Dr. Lionel S. Beale, F.R.S., a former President of the Microscopical Society, gave an interesting statement as to the methods of preparing specimens when examining the Microstructure of Iron and Steel.

Roberts-Austen in his book already quoted does just credit to the important work carried out in this Country by Professor J. O. Arnold, F.R.S., who had the great advantage of being in touch and collaborating with the late Dr. H. C. Sorby—in fact the mantle of Sorby descended upon him. Arnold commenced his work about 1890, and the World is under a debt of gratitude for the important results obtained by his valuable labours in this field of research.

Professor Arnold tells me that his first association with Sorby was about 1885 at the Natural Science Section of the Literary and Philosophical Society in Sheffield, where I also met him. When Arnold was appointed to the Chair of Metallurgy in the University of Sheffield in 1889 he persuaded Sorby to resume his micrographic work on Steel in conjunction with his (Arnold's) work on Chemical Analysis, Recalescence and Mechanical Testing, feeling sure that micro work was a vital factor, necessary to render more complete our knowledge of steel. However, Sorby stated he had so much on hand, and his eyesight was failing, that he was not able to take up the work again, but how glad he was to find that his pioneer work was considered to be helpful to Metallurgy. Sorby lent Arnold all his pioneer sections during his lifetime and in his Will left them to the Metallurgical Department of the University of Sheffield. Sorby also gave Arnold his various data and, on several occasions, went through his different sections, which, singular to say, were afterwards destined to be Arnold's for eleven years. Through the kindness of Professor Ripper these specimens are exhibited this evening.

It may be added that Sorby discovered at least five constituents of Steel, Stead three, and the Sheffield University—largely the work of Arnold himself—was responsible for many of the others now known to the World. It was also Arnold who determined the quantitative composition of Sorby's Pearlite and Hardenite.

Dr. J. E. Stead, F.R.S., also at an early date saw the great importance of this branch of investigation, and by his lucid papers and research work has greatly aided the progress of Metallography.

Osmond's unrivalled research work further established modern Metallography in 1895. He discovered successively the constituents of Quenched Steel and accurately determined the critical points of Iron. Moreover he had, along with Werth, previously described the cellular structure of metal. As Sauveur says, if Sorby was the pioneer of Metallography and Tchernoff its father, Osmond has been its torch-bearer.

The work of the Nomenclature Committee on Metallography is useful to those interested in this subject, and will be found in Vol. I

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of the Iron and Steel Institute Journal, 1902, comprising some twenty-three pages in its Glossary of Terms.

In addition to the main Societies, who have assisted in developing Microscopy, have been the following: The Sorby Scientific Society, comprising The Sheffield Microscopical Society, and The Sheffield Naturalist's Club, which were amalgamated on January 1st, 1918; the Quekett Microscopical Club; the Dublin Microscopical Club, and the Photomicrographic Society.

Special reference may be made to the excellent work of the Quekett Club, which is probably the most active Microscopical Club in any Country. Its Headquarters are in London, and Meetings are held from time to time. The present occupant of the Presidential Chair is Dr. A. B. Rendle, M.A., F.R.S.

SECTION III.—MODERN WORK ON MICROSCOPES, OBJECTIVES AND EYE-PIECES.

Mr. Conrad Beck, F.R.M.S., many years ago did valuable work on behalf of Microscopy in his Cantor Lectures before the Royal Society of Arts, 1907, on "The Theory of the Microscope." Previous to these Lectures, Mr. John Maynall, junr., gave two excellent series of Lectures on the same subject, entitled "The History of the Microscope." before the same Society.

An able Address was read by Mr. Joseph E. Barnard, now President of the Royal Microscopical Society, in February, 1919, on "The Limitations of Microscopy." Everyone interested in this subject should read the Address, which is divided into various subjects, dealing with dimensions met with in Microscopy, a discussion on the resolving power and limits of resolution and visibility; also descriptions of the Ultra-Microscope and of experiment sillustrating its use, together with a discussion of the advantages of ultra-violet light in ordinary Microscopy; and finally suggestions as to future lines of Research.

As this paper points out, the limit of resolution may be said to have been reached when it is not possible to distinguish the details of the specimen under examination. The limit of visibility is, however, lower than this, for, although no detail can be seen, the specimen can be made visible as a spot in the field of view.

The question of Resolution is touched upon, from which it appears that under the most favourable circumstances, the practical limit is reached when objects in a row are about ·20 micron (1 50,000 cm.) apart. If the body is less than this size under the best microscopic conditions now available no detail can be distinguished.

The Ultra-Microscope shows the presence of much smaller dimensions than those mentioned above, that is, as bright specks on a dark background, but it shows none of the internal features, and no matter what the shape or nature of the object under view, it always appears circular. The smallest particle observable, that is, in the Ultra-Microscope, is that of colloidal gold, about 5 micromillimeters (1 2,000,000 cm.) in diameter. Thus the Ultra-Microscope can distinguish particles about forty times smaller than those which can be resolved under the ordinary Microscope.

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Mr. Barnard showed in his Address that whilst the resolving power of a given instrument depends upon its design, it also depends upon the wave-length of the light used to illuminate the object under examination. Thus, if the object is illuminated with ultra-violet rays greater resolution still can be obtained, but, of course, the results are not directly visible and must be recorded photographically.

In a paper recently read before the Royal Microscopical Society by Colonel J. Clibborn, C.I.E., B.A., on " A Standard Microscope," it was stated by Mr. Conrad Beck that the Manufacturers of Microscopes worked under great difficulty during the War. It was not until after the 11th November, 1918, that any Microscopes were allowed to be made, all the Factories being fully engaged on other Optical Instruments. It is interesting to note, however, that these Firms are now spending large sums in manufacturing tools for the production of Microscopes, many of them to be made under the Specifications brought forward by the Committee on Microscopes appointed by the British Science Guild.

At the recent British Scientific Products Exhibition an excellent set of Exhibits was shown by the British Optical Instrument Manufacturers' Society, Ltd. Some dozen or more of the principal firms exhibited Optical Instruments and Glasses.

As pointed out in the valuable Catalogue of that Exhibition, the Optical Instrument-making Industry originated in most of its Branches in Great Britain. Newton, Young, Faraday, Clerk Maxwell and Rayleigh were the pioneers of Optics. The Achromatic Telescope was invented by Dolland, and the modern form of Achromatic Microscope by Lister. Let us therefore show that we are trying to be worthy successors of these great men.

The Optical Association has published an illustrated booklet on Scientific Instruments, which includes, with a brief description, the name of every known instrument both current and obsolete, together with a key to the British Makers. The Trade has set up a powerful Research Association and has participated in the inauguration of a Scheme of Education in Optical Engineering which is being developed by the Imperial College of Science and Technology at South Kensington. It may be mentioned that the Governing Body of the Imperial College of Science and Technology recognises the importance of Technical Optics in their relation to the needs of the Nation by providing in the Estimates of their new Scheme of Development the sum of £50,000 for expenditure on Land, Buildings and Equipment, and the sum of £4,000 annually for maintenance and carrying on the work.

Messrs. Chance Brothers commenced the manufacture of Optical Glasses in England in 1848. During the recent War they increased their output some twenty-fold. They make something like seventy different types of Optical Glasses together with a number of new types which have been recently introduced. They have rendered great service to our Empire.

Professor J. C. McLennan, F.R.S., of the University of Toronto, who was in England during the War, informed me that he had examined the Fluorite from South Africa and found it to be excellent in quality.

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If this Fluorite can be used in the manufacture of Glass suitable for High Power Objectives, then the South African source of supply should be borne in mind. It is also stated that Fluorite exists in Canada, and our Honorary Treasurer, Dr. Robert Mond, is investigating this matter,

The King recently visited the Leicester Works of Messrs. Taylor and Hobson, the famous Lens experts. He there saw the instruments by which vital errors of a few millionths of an inch are avoided, and had explained to him the principles of the use in this connection of light interference, which was first studied by Sir Isaac Newton in Soap Bubbles. This Firm also make the "Aviar" Lens, which through repeated calculations and readjustments of formulæ enabled the British Photographing Aeroplanes to beat the "Archies."

In a recent number of the "Scientific American Supplement" (August 30th, 1919), a statement is made that in spite of the traditional superiority of the German Optical Industry, during the War their Lenses proved distinctly inferior to those of French and English make. The English developed superior Lenses during and under the stress of the War.

In a perfect High Power Objective known as Apochromatic, it is desirable this should give :—

(*a*) *Full Resolution.*—The resolution increases with, and is a function of, Numerical Aperture. The number of lines to the inch which an objective will resolve, if perfect, may be calculated from the Numerical Aperture.

(*b*) *Good Definition.*—Which could be magnified by a × 28 eye-piece or its equivalent without breaking down.

(*c*) *A Perfectly Flat Field.*—This is never actually obtained.

(*d*) *Freedom from Chromatic Aberration.*

Achromatic Lenses generally give good definition and their field is often somewhat flatter than in that of the Apochromats. They do not, however, give such good resolution, and are only partially colour corrected. The latter failing makes them much less efficient than the Apochromats for photographic work.

The foreign 2 mm. Objective used in the Hadfield Laboratory is a very good one of its class. Its Numerical Aperture is 1.3, and therefore according to the formula of Professor Abbe, should, if perfect, resolve about 92,000 lines to the inch. I have had photographs taken by it which show 85,000 lines to the inch clearly resolved. Its definition begins to break down with an eye-piece magnification of about 15. For an Apochromat its field is very flat, and it is in this respect chiefly that we found it superior to other Apochromats we examined. Its colour correction is apparently perfect.

It may be added that Messrs. Watsons supplied to the Research Laboratory of my firm a very excellent 2 mm. Objective.

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In fact photomicrographs obtained with it seemed to possess almost equal quality to those from the best foreign objectives. Fig. 13 is a photomicrograph of a specimen of Steel taken with the above-mentioned foreign 2 mm. Apochromat, whilst Fig. 12 is a photomicrograph of the same section under exactly similar conditions, taken with the Watson 2 mm. Apochromat. It will be seen that there is very little to choose between the two photographs from the point of view of resolution and flatness of field. There is no doubt that English makers can, when required, produce Objectives at least equal in quality to the best foreign makes.

SECTION IV.—FERROUS METALLOGRAPHY.

Several excellent Works have been published on the important subject of Metallography, including "Physical Metallurgy," by Dr. Walter Rosenhain, F.R.S., which has proved of the highest service. No book, too, on the subject has been of greater use in the past than that by Professor Albert Sauveur, of Harvard University, "The Metallography of Iron and Steel." Great advances have been made since the date of its first publication, and in the second edition, 1916, it remains a standard work of reference and a model for books on a special subject —excellent matter, well printed and illustrated. The chapters are divided into Lessons, some twenty-four in all, commencing with the Study of Pure Metals; Pure Iron and Steel, up to High Carbon Percentages; the Effect of Impurities Upon Steel; Close Studies of Thermal Critical Change Points; the Effect of Annealing, Hardening and Tempering upon both ordinary and Special Alloy Steels, are considered. The Metallography of Cast Iron also receives attention. Various Apparatus for the Metallographic Laboratory, including the study of the Microscope itself, and the Apparatus, Illumination, Sources of Light, Condensers, and Photomicrographic Cameras; a description of the best Methods and Manipulations; also a most excellent nomenclature of the various Microscopic Constituents, including Austenite, Cementite, Martensite, Ferrite, Osmondite, Ferronite, Hardenite, Pearlite, Graphite, Troostite, Sorbite, Manganese Sulphide, and Ferrous Sulphide.

In words which deserve consideration by us all, so I quote them in full, Professor Sauveur in his Introduction and Remarks upon the Industrial Importance of Metallography, points out:

"Invaluable information is given by chemistry without which both the physicist and the metallurgist would be in utter darkness, but this science throws little or no light upon the anatomy of living or inanimate matter. Its very methods, which call for the destruction of the physical structure of matter, show how incapable it is to render assistance in this, our great need.

The parallel drawn here between metals and living matter is not fantastic. It has been aptly made by Osmond, who said rightly that modern science was treating the industrial metal like a living organism, and that we were led to study its anatomy, that is, its physical and chemical constitution; its biology, that is, the influence

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exerted on its constitution by the various treatments, thermal and mechanical, to which the metal is lawfully subjected; and its pathology, that is, the action of impurities and defective treatments upon its normal constitution.

Fortunately Metallography does more than reveal the proximate composition of metals. It is a true dissecting method which lays bare their anatomy—that is, the physical grouping of the proximate constituents, their distribution, relative dimensions, etc., all of which necessarily affect the properties. For two pieces of steel, for instance, might have exactly the same proximate composition—that is, might contain, let us say, the same proportion of pearlite and ferrite, and still differ quite a little as to strength, ductility, etc., and that because of a different structural arrangement of the two proximate constituents; in other words, because of unlike anatomy.

It is not to be supposed that the path trodden during the last score of years was at all times smooth and free from obstacles. Indeed, the truth of the proverb that there is no royal road to knowledge was constantly and forcibly impressed on the minds of those engaged in the arduous task of lifting metallography to a higher level.

Its short history resembles the history of the development of all sciences. At the outset a mist so thickly surrounds the goal that only the most courageous and better equipped attempt to pierce it and perchance they may be rewarded by a gleam of light. This gives courage to others, and the new recruits add strength to the besieging party. Then follow the well-known attacking methods of scientific tactics and strategy, and after many defeats, and now and then a victorious battle, the goal is in sight, but only in sight and never to be actually reached, for in our way stands the great universal mystery of nature: what is matter? what is life?

Nevertheless there is reward enough for the scientist in the feeling that he has approached the goal, that he has secured a better point of vantage from which to contemplate it. The game was worth the candle, and if scientific workers must necessarily fail in their efforts to arrive at the true definition of matter, whatever be the field of their labour, they at least learn a great deal concerning the ways of matter, and it is with the ways of matter that the material world is chiefly concerned. Hence the usefulness of scientific investigation, hence the usefulness of metallography."

Among the many workers who have contributed to the progress of Metallography may be mentioned:—Arnold, Benedicks, Belaiew, Brearley, Carpenter, H. Le Chatelier, Campbell, Desch, Edwards, Elliot, Guillet, Gulliver, Giolitti, Hatfield, Honda, Howe, Humfrey, Hudson, Zay Jeffries, Law, Martens, McCance, Osmond, Portevin, Roberts-Austen, Rosenhain, Robin, Sorby, Sauveur, Stead, Thompson, Werth.

In the valuable Pocket Encyclopædia on "Iron and Steel" by Mr. Hugh P. Tiemann, B.S., A.M., with an introduction by Professor H. M. Howe, some thirty pages are devoted to Metallography. The book contains a most excellent summary of the terms used in this Branch of the Science of Metallurgy, treating of the constitution and structure of Metals and Alloys, also their relation to physical properties.

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Tiemann says that originally the term Metallography concerned principally the visual examination of the structure of metals, and hence was divided into Microscopic Metallography, or, briefly, Micrometallography, where Microscopes were used to secure high magnifications, and Megascopic, Macroscopic or Macro-Metallography, where the naked eye or very low magnifications were used. The terms Microscopy and Micrography are also used.

With reference to Metallographic Examination, Tiemann considers that the methods employed may be classified into :—

(1) OPTICAL ANALYSIS: Determining the Constituents, structures, forms, appearances, etc., by the eye alone or assisted by suitable magnifying devices.

(2) THERMAL ANALYSIS: A Study of the nature of metals and alloys by means of heating and cooling curves, changes in specific heat, etc.

(3) MAGNETIC ANALYSIS: Determination of changes in nature affecting the magnetic properties.

(4) PHYSICAL ANALYSIS: Determination of the properties by the usual methods of testing.

(5) CHEMICAL ANALYSIS: Both proximate and ultimate; generally in conjunction with one of the other methods.

He defines the Microscope as follows :—

(*a*) A simple Microscope is one which has only one Lens or set of Lenses ; a compound Microscope has two such systems of Lenses, one near the object (Objective) and the other near the eye of the observer (Eyepiece).

(*b*) The binocular Microscope consists of two instruments mounted to give a stereoscopic (perspective) view.

As regards the minute nature of matters forming metals and alloys of metals, an interesting statement is made by Mr. Zay Jeffries, D.Sc., Cleveland, U.S.A., who, when speaking of the ageing of the non-ferrous metal known as Duralumin, in his paper on "The Micro-mechanism of the Ageing of Duralumin," says that when it is cooled from 500° C. in a furnace, globules of $CuAl_2$ large enough to be seen easily with a high power Microscope, are formed. In the same sample, however, some globules are so small as to be hardly distinguishable, and others too small to be resolved are suggested by the non-uniformity of the surface appearance of the section. When it is considered that the smallest globule of $CuAl_2$ resolvable with a high power Microscope contains about 2,000,000,000 molecules, it is evident that with rapid cooling sub-microscopic particles of $CuAl_2$ must be present in large numbers ; in fact, after quenching, the average size of a particle must be sub-microscopic. The whole phenomenon of ageing must, therefore, involve changes which cannot be studied directly with a Microscope.

The same author has devoted a great amount of time to the study of grain sizes and their measurement in metals. He has contributed several papers to the Faraday and other Societies in this country. Much valuable information is to be found in the work done by Dr. Zay Jeffries.

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PREPARATION OF SPECIMENS AND ETCHING.—In the preparation of specimens for micro-examination great skill and ingenuity have been displayed by numerous investigators from the time of Sorby onwards.

When it is considered that a maximum magnification has now been reached of about 8,000, the difficulties to be overcome will be readily recognised. Supposing the surface of one side of a cube, say one twenty-fifth of an inch square, to be under examination, this has meant that the area under observation has been multiplied or magnified to a surface of say 30 ft. square, or about 900 square feet. It will be seen how the slightest scratch or groove, imperfect polishing, bad etching, or other defect will at once interfere with the desired results being obtained.

In this connection I should like also to call attention to an interesting Paper read by Sir G. T. Beilby, F.R.S., before the Royal Society in February, 1914, entitled "Transparence or Translucence of the Surface Film produced in Polishing Metals." Some beautiful Photomicrographs are there shown, photographed by a 3 mm. Oil immersion Lens of 1.4 N.A. The thickness of the films covering the slight Pits on a Copper surface was stated by Sir George to be probably of the order of 10 to 20 micro-millimetres ($\frac{1}{2.500.000}$ to $\frac{1}{1.200.000}$ inch).

Although if it was possible to get raw surfaces free from all grooves, scratches, and other blemishes, some structure would be developed, it must be remembered that not even the finest polishing will display structure, therefore etching must be employed.

The etching accomplishes two things: it removes the amorphous layer, and then attacks the various constituents differently. The products of the etching attack usually differ in appearance more than the original constituents.

For high power the etching must be very light, that is, the time of etching must be short. A 5 per cent. solution of picric acid in alcohol gives the best results. The perfect flatness of the polished surface must be retained, and only the lightest possible etching is given. In low power work the etching is fairly strong in order to obtain contrast between the light and dark portions.

As regards the effect of different kinds of etching, I invite attention to Photomicrographs, Figs. 9, 10 and 11. These are from a Gun Tube Steel containing .42 per cent. Carbon, .74 per cent. Manganese, and representing material as forged, that is without further treatment.

Fig. 9 was etched with 5 per cent. Picric Acid in Alcohol.
Fig. 10 was etched with 5 per cent. Nitric Acid in Alcohol.
Fig. 11 was etched with 5 per cent. Solution Meta-Nitro-Benzol-Sulphonic Acid.

The structure shows grains of Ferrite on a ground mass of Pearlite and the Photomicrographs prove that the Structure developed is independent of the particular etching reagent used. The number of etching reagents might be extended on this work with practically the same results in each case. Most Alloy Steels, for example, Manganese Steels, quenched and tempered, Nickel Chromium and other Steels,

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require extraordinary care in the etching or otherwise the structure will vary considerably and be misleading. Some alloys, for example Steel containing high percentage of Nickel, are not attacked by any ordinary etching reagent.

All honour to Sorby, the man who led the way in this branch of Science, and started us, who are to-day benefiting in such a remarkable manner from the knowledge he first originated and obtained in this important and complex branch of Science. All honour, too, to the band of willing workers who have accomplished such great progress, and who have surmounted the many difficulties in their path.

SECTION V.—STANDARD MAGNIFICATIONS FOR PHOTOMICROGRAPHS.

The question of the Standardisation of Magnifications for Photomicrographs of Metals and Alloys has been given a certain amount of discussion both in this Country and in America.

Committee E-4 of the American Society for Testing Materials has, in fact, drawn up tentative "Definitions and Rules governing the Preparation of Micrographs of Metals and Alloys," which include Standard Magnifications for general use, and Ferrous and Non-ferrous Metals. I have brought this matter before the British Engineering Standards Association, who are considering the subject. The Institute of Metals in this Country in its "Notes for Authors" also specify certain Standard Magnifications which it is desired Authors should use.

Whilst not wishing in any way to hamper the Research Worker, there are reasons why it seems strongly advisable that for general purposes Standard Magnifications should be adopted for the Photomicrographs. Very little quantitative data is forthcoming from the micro-examination of metals. Where the grain size can be determined, this is often distinctly useful and worth recording. For the most part, however, the Microscopist is dependent on a trained eye, resulting from prolonged experience in the examination of microstructures to aid him in their interpretation. It would seem reasonable, therefore, that the magnifications used should be standardised and as few as possible, in order that comparisons between the structures of different specimens may be facilitated.

I would therefore like strongly to urge that the various Societies interested in Metallography should join in drawing up rules governing the reproduction of photomicrographs, which should be of certain Standard Magnifications and naturally should be reproduced full size.

Surely there is every reason for having an International Standard; at any rate, Great Britain and America could work together. It might well, indeed, be made a matter for Allied consideration, or one for consideration in connection with the movement for the formation of International Unions in which the Conjoint Board of Scientific Societies is interesting itself.

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SECTION VI.—CRYSTALLOGRAPHY.

As crystallography is, if not directly then indirectly, related to the work of the microscope, I have asked my friend, Dr. A. E. H. Tutton, F.R.S., the eminent crystallographist, to communicate suggestions to this Symposium by way of a Paper or to the Discussion from his point of view.

During the recent Meeting at Bournemouth of the British Association, Miss Nina Hosali, B.Sc. of the University of London, exhibited interesting Models of Crystals. This worker has most kindly submitted her collection this evening and I am sure they will be found useful.

As explained by Miss Hosali, the object of these models is to illustrate :—

(*a*) The forms possible to crystals.
(*b*) The different kinds of symmetry possessed by these forms.
(*c*) How the forms are referred to crystallographic axes.

Each model illustrates one of the thirty-two classes of symmetry, and represents several crystal forms correctly orientated with regard to crystallographic axes, the latter being shown by black threads. A model consists in the first place of a glass envelope whose shape is hat of some simple crystal form, and within this envelope two or three other forms are represented by means of coloured silk threads stretched over frameworks of thin copper wire. By this means it is easy to make the forms intersect if necessary, and they are readily distinguished from one another by the use of differently coloured threads.

The symmetry elements of the class represented by any model are shown as follows :—

(*a*) The traces of the Planes of Symmetry on the Glass envelope are shown by steel wires.

(*b*) Axes of Symmetry are shown by white threads.

The set of 24 models exhibited represents 21 out of the 32 classes and over 70 different forms. In many cases different varieties of the forms may be produced by rotating or inverting the models, or by reflecting them in a mirror, and when these modifications are taken account of, the number of the forms shown is brought up to about 140.

It may be interesting to add that there has been recently developed and described by the Research Committee of the American Society of Mechanical Engineers an instrument called the Microcharacter (from the Greek—to engrave or scratch on a small scale). This instrument determines that characteristic of a crystal which is the combination of three of the five fundamental conceptions of hardness, namely, the combined effect of cutting, scratch, and penetration hardness. It can be employed for determining the hardness of the micro-constituents of steel and should be very useful to the Metallographist. This Apparatus should be very useful to the Metallographer, as the

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point used is practically sharp under a magnification of no less than 2000 diameters. By this method these combined characteristics can be obtained for any individual crystal, a point of great importance.

SECTION VII.—THE ULTRAMICROSCOPE.

Much study has been given to the Ultramicroscope, which was introduced about the year 1905 by Siedentopf and Zsigmondy.

In an article which appeared in "The Scientific American," October 2nd, 1915, it was stated that the limits of microscopic observation with direct illumination is about $\frac{1}{4.000}$ mm. and with oblique illumination by means of violet rays and with the aid of monobromated naphthalene immersion $\frac{12}{100.000}$ mm. The observation of particles below this may be termed ultramicroscopic. According to Siedentopf, particles may be perceived which have a diameter of about $\frac{4}{1.000.000}$ to $\frac{6}{1.000.000}$ mm. These are magnitudes which approach very closely to molecular dimensions of complicated compounds, in some cases even attain them.

According to O. E. Meyer, the molecule of Hydrogen has a diameter of $\frac{1}{10.000.000}$ mm., while according to Jaeger, the molecule of (*a*) ethyl-alcohol has a diameter of $\frac{5}{10.000.000}$ mm.; (*b*) chloroform has a diameter of $\frac{8}{10.000.000}$ mm. According to Lobry de Bruyn, the molecule of starch has a diameter of $\frac{5}{1.000.000}$ mm. Consequently the molecule of starch must be within the reach of ultramicroscopic perception.

The investigator has therefore before him, subject to increased intensity of light and dark field, the possibility of seeing molecules which seemed beyond reach of human sight, and the hope of following the play of their attractive and repellant forces. The brightness of ultramicroscopic particles begins to decline with the 6th power of the diameter.

If it should prove possible to obtain this deeper insight into the form and structure of matter, a positive service will be done to philosophy permitting of the observation of particles which were formerly far below the limits of ordinary microscopic observation. If the methods which it renders possible can be extended and applied to Metallurgy, then the Metallurgist will doubtless be possessed of still further means to enable him to advance further our knowledge of the structure of metals and their alloys.

SECTION VIII.—CONCLUSION.

I must now bring these remarks to a close. The subject is a fascinating one, and it has been a labour of love to trace the History of the Microscope and its great development into the wonderful Scientific Instrument of to-day, capable of resolving even over 100,000 lines per inch.

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If Sorby could have been with us this evening it would be a special satisfaction to him to see the child of his brain grown to the giant it now is, I mean in the application of the Microscope to the examination of Metals and their Alloys. In a separate communication entitled "The Great Work of Sorby, of Sheffield," I have dealt briefly with his Researches in this field.

In addition to this present Address, I am contributing to the Symposium a Paper on the Faraday Society and its Work; also jointly with Mr. T. G. Elliot, F.I.C., a Paper on "Photomicrographs of Steel and Iron Sections at High Magnification," as well as a Bibliography from 1665 down to the present time, which although not claimed to be complete may be found useful to those interested.

I trust that in each of these contributions will be found some information that may be of interest and give encouragement to pursue our Researches in this valuable field of Scientific Investigation.

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SECTION IX.– BIBLIOGRAPHY OF THE CHIEF LITERATURE RELATING TO MICROGRAPHY.

Date.	Title.	Author.	Publication.	Country.	Description.
1665	Micrographia: or some Physiological descriptions of Minute bodies made by Magnifying Glasses, with observations and Inquiries thereupon	R. Hooke		England	Book
1668	Account of Divinis' Compound Microscope		Phil. Transactions, No. 42	England	Paper
1718	Descriptions et Usages de plusieurs Nouveaux Microscopes, tant Simples que Composez	L. Joblot		France	Paper
17[illegible]8	Essays on the Microscope (Bibliography)	G. Adams		England	Paper
1851	On the Microscopical Structure of the Calcareous Grit of the Yorkshire Coast	Dr. H. C. Sorby	Quarterly Journal Geol. Soc. VII, 1851, pp. 1–6	England	Paper
Mar. 1854	On the Construction of the Compound Achromatic Microscope	C. Brooke	Royal Inst., Great Britain	England	Paper
1856	On the Theory of the Origin of Slaty Cleavage	Dr. H. C. Sorby	Phil. Mag. XII, 1856, pp. 127–129	England	Paper
1856	On the Microscopical Structure of Mica Schist	Dr. H. C. Sorby	Brit. Assoc. Report, 1856 (pt. 2), p. 78	England	Paper
	The History of the Microscope	J. Maynall, Jnr.	Royal Society of Arts	England	Paper
1857	On Some Peculiarities in the Microscopical Structure of Crystals, Applicable to the Determination of the Aqueous or Igneous Origin of Minerals and Rocks	Dr. H. C. Sorby	Abstracts of the Proc. of the Geol. Soc., Dec. 2nd, 1857	England	Paper
1858	On the Microscopical Structure of Crystals indicating the Origin of Minerals and Rocks	Dr. H. C. Sorby	Quarterly Journal Geol. Soc.	England	Paper
1863	On the Microscopical Structure of Mount Sorrel Syenite, Artificially Fused and Cooled Slowly	Dr. H. C. Sorby	Geol. and Polytechnic Society of the West Riding of Yorkshire. IV, May 28th, 1863.	England	Paper

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Date.	Title.	Author.	Publication.	Country.	Description.
1864	On a New Method of Illustrating the Structure of Various Kinds of "Blister Steel" by Nature Printing	Dr. H. C. Sorby	Sheffield Lit. and Phil. Soc., Feb., 1864	England	Paper
1864	On Microscopical Photographs of Various Kinds of Iron and Steel	Dr. H. C. Sorby	Brit. Assoc. Rep., 1864, pt. II, p. 189	England	Paper
1864	(*a*) On the Conclusions to be Drawn from the Physical Structure of some Meteorites	Dr. H. C. Sorby	Brit. Assoc. Rep., 1864, p. 70	England	Paper
1864	(*b*) On the Microscopical Structure of Some Meteorites	Dr. H. C. Sorby	Royal Soc. Proc., XIII, 1864, pp. 333–334. Phil. Mag. (4 ser), XXVIII, pp. 157–159. Brit. Assoc. Rep., 1865, (pt. 1), pp. 139–140.	England	Paper
1864	On Microscopical Photographs of various kinds of Iron and Steel. Part II, page 189		British Assoc. Report	England	Report
1865	On the Microscopical Structure of Meteorites and Meteoric Iron. Vol. XIII		British Assoc. Report and Proceedings Royal Society	England	Report
1868	Iron and Steel Manufacture	F. Kohn		England	Book
1868	How to work with the Microscope. Microscopical Structure of Iron and Steel	Dr. L. Beale		England	Paper
1870	On the Application of the Microscope to the Study of Rocks	Dr. H. C. Sorby	Monthly Microscopical Journal, Sept. 1st, 1870, pp. 148–149	England	Paper
1875	Limit of the Powers of the Microscope	Dr. H. C. Sorby	Journal of the Royal Micro. Society, 1875	England	Paper
1876–7	Presidential Address	Dr. H. C. Sorby		England	Address
1877	Note on the Ultimate Limit of Vision	Dr. Dallinger	Journal of the Royal Micro. Soc., Vol. 17, 1877, page 224	England	Paper
1878	The Microscopical Examination of Iron	Martens		Germany	Paper
Oct. 1882	Lecture delivered in Firth's College, Sheffield, on "The Microscopical Structure of Iron and Steel"	Dr. H. C. Sorby	The Engineer	England	Lecture

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Date.	Title.	Author.	Publication.	Country.	Description.
1886	On the Application of Very High Powers to the Study of the Microscopical Structure of Steel	Dr. H. C. Sorby	Journal of the I.S.I., Vol. I, 1886, pp. 140–144	England	Paper
1886	Cantor Lectures on the Microscope.	J. Mayalb, Jun.		England	Paper
1887	On the Microscopical Structure of Iron and Steel	Dr. H. C. Sorby	Journal of the I.S.I., Vol. I, 1887, pp. 1–34	England	Paper
1887	The Microscopical Structure of Iron and Steel. (p. 255)		Journal of The Iron & Steel Institute	England	
Apr. 1889	Progress in the Photographic reproduction of the Micro-Structure of Iron	Dr. Wedding	Stahl und Eisen	Germany	Paper
Feb. 1892	Recherches Microscopiques sur la Structures des Metaux	F. Osmond		France	Paper
1896	Micro-Structure of Iron and Steel	Prof. A. Martens		Germany	Paper
1896	Bibliography of Articles in German Publications on Microscopy, 1880—1896	A. Martens		Germany	Cuttings
1896	Das Mikoskop	B. J. Petri		Germany	Book
1897	Microscopy (Vol. I., 42)	Dr. J. E. Stead	Jnl., I. & S. I.	England	Cutting
1898	Microscopy. (73, 714)	Heycock & Neville	Trans. Chem. Soc.	England	Cutting
1898	Fifty Years of Scientific Research	Dr. H. C. Sorby	Sheffield Lit. and Phil. Soc. Rep. 1898, pp. 13-21	England	Paper
Aug. 1899	Practical Microscopic Analysis	C. H. Ridsdale	Iron & Steel Inst.	England	Paper
1899	Mitteilungen der Königl. Technischen Versuchsanstalt. (XVII. 73)	Martens & Heyn		Germany	Cutting
Jan. 1900	The Microstructure of Steel	E. Heyn	Stahl und Eisen	Germany	Paper
1900	Henry Clifton Sorby—A Biographical Sketch		The Metallographist, April 1900	U.S.A.	Paper
Sept. 1900	La Technique de la Métallographie Microscopique	H. de Chatelier	Bulletin Soc. d'Encouragement	France	Cutting
1900	La Cristallographie du Fer	F. Osmond & G. Cartaud	Annales des Mines, 1900.	France	Paper
1900	The Crystalline Structure of Metals ...	Ewing & Rosenhain	Phil. Trans. Roy. Soc., 1900.		
1900	On Microscopy. (194a, 201)	Heycock & Neville	Phil. Trans.	England	Cutting

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Date.	Title.	Author.	Publication.	Country.	Description.
1900	On Microscopy. (II, 137)	Stead	Jnl. I.S.I.	England	Cutting
Jan. 1901	On Microscopy. (Vol. IV., No. 1)	Le Chatelier	The Metallographist	England	Cutting
Dec. 1901	Microscopical Examination of the Alloys of Copper and Tin	W. Campbell	Inst. Mech. Eng.	England	Paper
1901	On Microscopy. (p. 277)	Osmond	Etudes des Alliages	France	Cutting
1901	On Microscopy. (p. 421)	Le Chatelier	Etudes des Alliages	France	Cutting
Dec. 1902	The Microscope in the Determination of the Properties of Steel	A. Sauveur	Eng. Soc. of West Pennsylvania	U.S.A.	Paper
1902	Report on the Nomenclature Committee on Metallography		Journal of the I.S.I., Vol. I, 1902	England	Paper
1902	Microstructure of Hardened Steel	J. O. Arnold & A. McWilliam	Iron & Steel Inst.	England	Paper
Sept. 1903	Diseases of Steel	C. H. Ridsdale	Iron & Steel Inst.	England	Paper
Oct. 1904	Notes on the Metallography of Steel	B. Stoughton	Am. Soc. Civil Eng.	U.S.A.	Paper
Dec. 1904	Microscopic Observations in Naval Accidents	T. Andrews	Engineering	England	Cutting
1904	Troostite	H. C. Boynton	Iron and Steel Inst.	England	Paper
1904	Sur le Technique de la Métallographie Microscopique	H. Le Chatelier		France	Paper
1904	Verhandlungen Vereins zur Beförderung des Gewerbefleisses. (p. 235)	Heyn		Germany	Cutting
Feb. 1905	High Power Microscopy	J. W. Gordon	Royal Institution	England	Paper
1905	On Microscopy. (2; 528)	Le Chatelier	Revue de Métallurgie	France	Cutting
1906	Des Applications Pratiques de la Metallographie Microscopique	H. le Chatelier	Congres de l'Assoc. International	Belgium	Paper
1906	On Microscopy. (36. II, 142)	Giolitti	Gazzetta	Italy	Cutting
1906	On Microscopy. (pp. 146-155)	Rosenhain	Jnl. R. Micro. Soc.	England	Cutting
1906	An Improved Form of Metallurgical Microscope	Rosenhain	Jnl. R. Micro. Soc.	England	Paper
1906	Principles of Microscopy	Wrights		England	Book
1906	"Cantor" Lecture	Beck		England	Book
May 1908	Application of Colour Photography to Metallography	E. F. Law	Mechanical Engineer	England	Cutting
1908	On Microscopy. (38. II, 352)	Giolitti	Gazetta	Italy	Cutting
1908	On Microscopy. (III, p. 22)	Stead	Jnl. I.S.I.	England	Cutting
1908	Introduction to Metallography....	Goerens		England	Book

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Date.	Title.	Author.	Publication.	Country.	Description.
1908	An Introduction to the Study of Metallurgy (including Bibliography)	Sir W. Roberts-Austen	Metallography	England	Book
June 1909	Metallographic Observations in Vacuo at High Temperatures	P. Oberhoffer	Metallurgie	Germany	Paper
1909	On Microscopy. (VI., 320)	Benedicks	Metallurgie	Germany	Cutting
June 1910	The Microscope and some of its Applications to Metallurgy	W. Tassin	Iron Age	U.S.A.	Cutting
June 1910	Apparatus for the Microscopical Examination of Metals	A. Sauveur	Am. Soc. for Testing Materials	U.S.A.	Paper
July 1910	Apparatus for observing Metals under Strain		Physical Society of London	England	Paper
1910	Catalogue of the Library		Royal Microscopical Society	England	Catalogue
1910	Pocket Encyclopædia on Iron and Steel	Hugh P. Tiemann		England	Book
1910	Metallography	Dr. C. H. Desch		England	Book
May 1911	Metallography and its Industrial Importance	A. Sauveur	Met. & Chem. Eng.	U.S.A.	Cutting
July 1911	The Utility of the Metallographic Microscope	J. Aston	Jnl. Ind. and Eng. Chemistry	U.S.A.	Paper
1911	The Hard and Soft State in Metals	Martens		Germany	Cutting
Jan. 1912	Micro-Metallography and its Practical Application	Dr. J. E. Stead	Iron & Steel Inst.	England	Paper
May 1912	The Inner Structure of Simple Metals....	Sir J. A. Ewing	Inst. of Metals	England	Paper
1912	The Intercrystalline Fracture of Iron and Steel	J. C. W. Humfrey	Iron & Steel Inst.	England	Paper
1912	Traité de Métallographie	Robin		France	Book
1913	Presidential Address to the Royal Microscopical Society	Prof. H. G. Plimmer	Journal of the Micro. Society, 1913	England	Address
May 1913	The Tenacity, Deformation and Fracture of Soft Steel at High Temperatures	W. Rosenhain & J.C.W.Humfrey	Iron & Steel Inst.	England	Paper
May 1913	Nyttan at Mikrokopiens Anvandning inom Jarnhandteringen	Ivar Barthen		Sweden	Paper
Aug. 1913	Early Use of the Microscope at Iron and Steel Works	P. Kreuzpointner	Iron Age	U.S.A.	Cutting

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Date.	Title.	Author.	Publication.	Country.	Description.
Sept. 1913	Metallographic Testing		Bur. of Standards	U.S.A.	Circular
Sept. 1913	On a Method of Preparing Sections of Steel for Microscopic Examination	A. Campion & J. M. Ferguson	Iron & Steel Inst.	England	Paper
Oct. 1913	On the Microscopical Examination of Metals	H. Hannemann & K. Endell	Stahl und Eisen	Germany	Cutting
1913	The Intercrystalline Cohesion of Metals	Dr. W. Rosenhain & D. Ewen	Inst. of Metals	England	Paper
1913	Microscopic Analysis of Metals	Osmond		France	Book
1913	Photo-Micrography	Hinde & Randle		England	Book
Feb. 1914	First Sorby Lecture. (Including Bibliography of Important Papers by Dr. H. C. Sorby—14 in number)	W. G. Fearnsides	Sheffield Society of Eng. & Met.	England	Paper
Apl. 1914	A Microscopic Study of Electrolytic Iron	O. W. Storey	Am. Electro-Chemical Society	U.S.A.	Paper
June 1914	La Metallographie Microscopique	H. Le Chatelier	Rev. de Métallurgie	France	Cutting
1914	Introduction to Physical Metallurgy	Rosenhain		England	Book
1914	Lehrbuch der Metallographie	Tammann		Germany	Book
1914	On Microscopy. (Vol. I)	Rosenhain & Haughton	Jnl. I.S.I.	England	Cutting
1914	Notes on the Early History of the Microscope	Dr. Chas. Singer	Royal Society of Medicine, 1914	England	Paper
1914	The Solidification of Metals	Dr. C. H. Desch	Inst. of Metals	England	Report
Oct. 1915	The Ultramicroscope		Scientific American Supplement No. 2074	America	Paper
Mar. 1915	Appliances for Metallographic Research	W. Rosenhain	Inst. of Metals	England	Paper
1915	Einführung in die Metallographie und Wärmebehandlung	Hanemann	Gebrüder Borntraeger	Germany	Book
1915	The Dawn of Microscopical Discovery ...	Dr. Chas. Singer	Jnl. Royal Micro. Soc., 1915	England	Paper
Feb. 1916	The Requirements of the Bureau of Ordnance	H. E. Cook	Am. Inst. of Mining Engineers	U.S.A.	Paper
Feb. 1916	Prolegomena towards a Study of the Progress and Development of Vision and and Definition under the Microscope (1673-1848).	E. Heron Allen & C. F. Rousselet	Jnl. R. Micro. Soc.	England	Paper

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Date.	Title.	Author.	Publication.	Country.	Description.
Apl. 1916	Precision Method of Uniting Optical Glass. The Union of Glass in Optical Contact by Heat Treatment	R. G. Parker & A. J. Dalladay	Faraday Society	England	Paper
1916	Metallography of Steel and Cast Iron	Howe		U.S.A.	Book
1916	Metallography and Heat Treatment of Iron and Steel	Sauveur		U.S.A.	Book
1916	Physico-Chemical Properties of Steel	Edwards		England	Book
1917	The Microscope	Gage			Book
1917	Microscopic Examination of Steel	Fay			Paper
1918	Précié de Métallographie, Microscopie et de Macrographie	Guillet & Portevin		France	Paper
1919	A Standard Microscope	Col. J. Clibborn	Journal of the Royal Micro. Soc., 1919	England	Paper
1919	The Micro Mechanism of the Ageing of Duralumin	Zay Jeffries	Institute of Metals	England	
Feb. 1919	The Limitations of Microscopy	Dr. J. E. Barnard, F.R.M.S.	Journal of the Royal Micro. Soc., March, 1919	England	Address
1919	The Solidification of Metals	Dr. C. H. Desch	Inst.of Metals	England	Report

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Dr. H. C. SORBY, F.R.S., of Sheffield.

President of the Royal Microscopical Society in 1875-7.

FIGURE 1.

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DR. W. H. DALLINGER, F.R.S.

FIGURE 2.

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FIGURE 3.

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FIGURE 4.

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Hadfield.—5.

MICROGRAPHIA:

OR SOME

Physiological Descriptions

OF

MINUTE BODIES

MADE BY

MAGNIFYING GLASSES.

WITH

OBSERVATIONS and INQUIRIES thereupon.

By *R. HOOKE*, Fellow of the ROYAL SOCIETY.

Non possis oculo quantum contendere Lynceus,
Non tamen idcirco contemnas Lippus inungi. Horat. Ep. lib. 1.

LONDON, Printed by *Jo. Martyn*, and *Ja. Allestry*, Printers to the ROYAL SOCIETY, and are to be sold at their Shop at the *Bell* in S. *Paul's* Church-yard. M DC LX V.

Rob: Hooke:

FIGURE 5.—Representing the front page of Hooke's "Micrographia," published in 1665.

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FIGURE 6.

Point of a needle, magnified.
Reproduced from a Drawing made by Hooke in the year 1665.

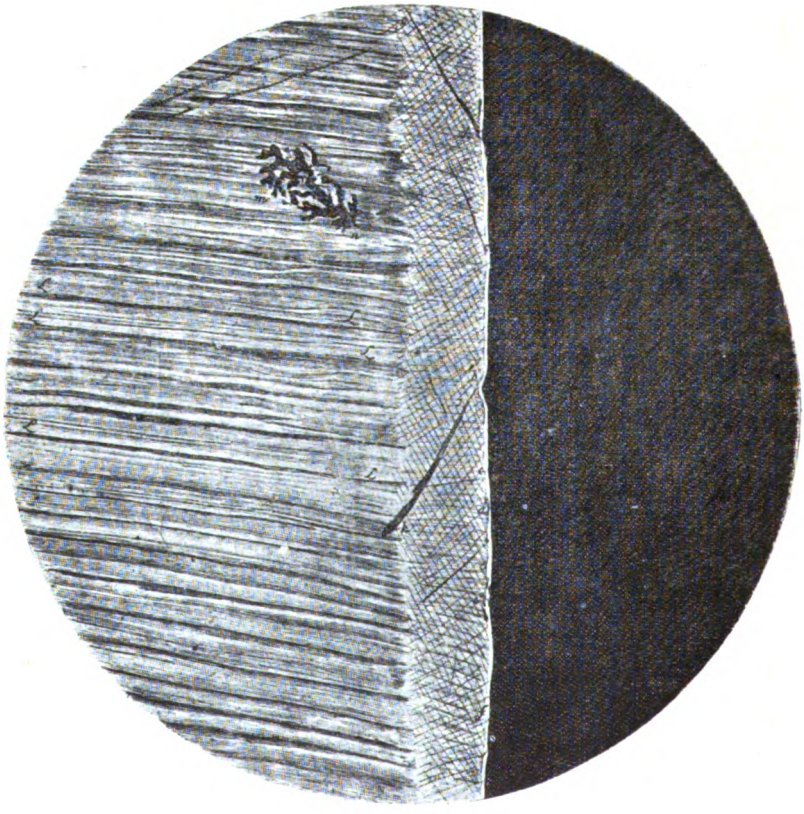

FIGURE 7.

Edge of a razor, magnified.
Reproduced from a Drawing made by Hooke in the year 1665.

These Figures are about three-fifths size of Hooke's enlargement.

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FIGURE 8.

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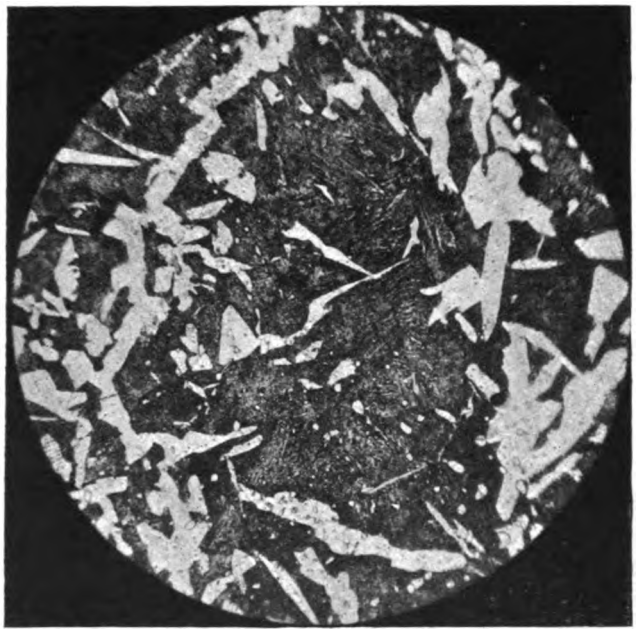

Magnification 100.
Etched with 5% Picric Acid in Alcohol.

Magnification 100.
Etched with 5% Nitric Acid in Alcohol.

FIGURES 9 AND 10.

Photomicrographs showing that the Structure of a Gun Tube Steel is independent of the etching reagent.

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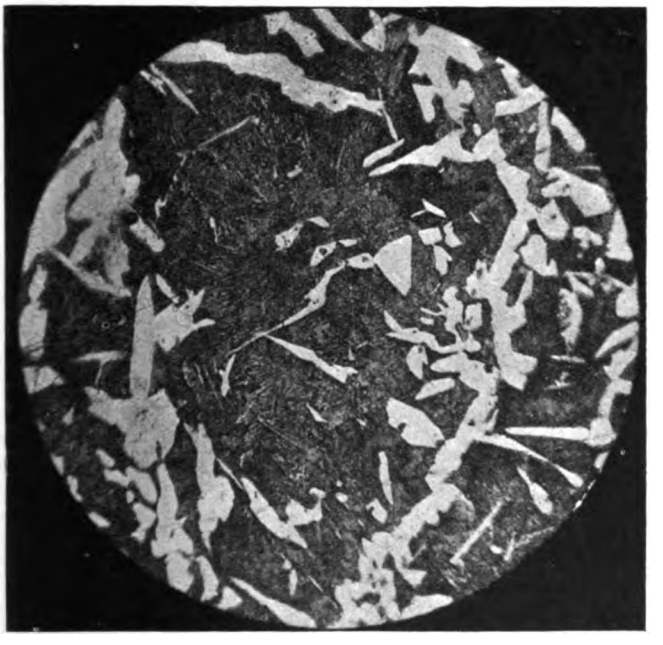
Analysis: C. .42, Mn. .74%.

Treatment: As Forged.

The Structure shows grains of Ferrite on a ground mass of Pearlite.



Magnification 100.

Etched with 5% Solution Meta-Nitro-Benzol-Sulphonic Acid.

FIGURE 11.

Photomicrographs showing that the Structure of a Gun Tube Steel is independent of the etching reagent

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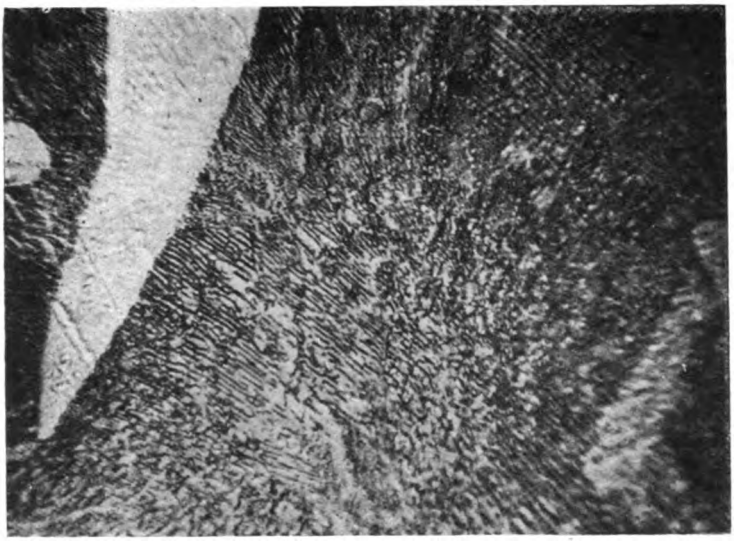
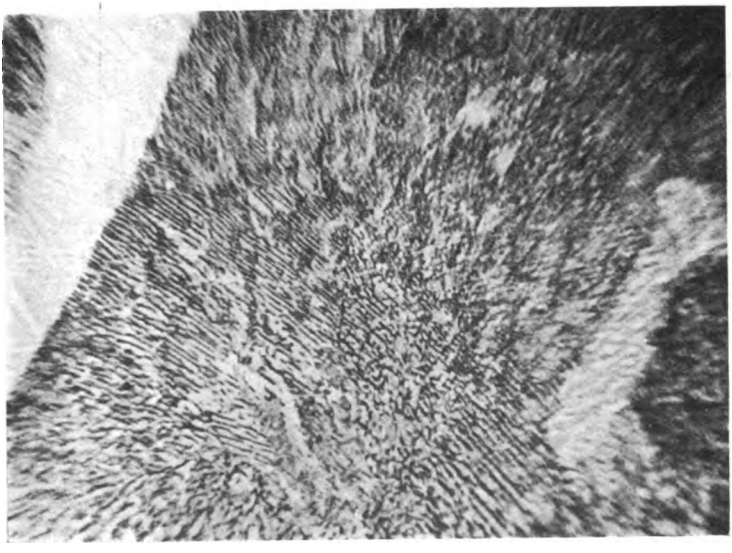


Foreign 2 mm. Apochromat.
Magnification 1,500.
FIGURE 13.



Watson 2 mm. British-made Apochromat.
Magnification 1,500.
FIGURE 12.

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THE PRESENT POSITION AND THE FUTURE OF THE MICROSCOPE—A GENERAL SURVEY.

By J. E. Barnard,

President of the Royal Microscopical Society.

Mr. J. E. Barnard, President of the Royal Microscopical Society, then delivered an address, of which the following is a condensed report, in which he indicated future lines of development in microscope design and in microscopy.

On behalf of the Royal Microscopical Society, I trust I may be allowed to convey to Sir Robert Hadfield the expression of my great appreciation of the efforts he has made, resulting in the holding of this Symposium. The subject is one that is in need of discussion; but, had it not been for Sir Robert's scientific insight and energy, it is unquestionable that the meeting would never have taken place. As the time that is allotted to me is of necessity short, it will be impossible to give anything like a full survey of the subject of microscopy. I shall, therefore, be compelled to limit myself to such points as appear to me to be of interest, although I admit that I am not always selecting the ones of greatest importance.

An examination of the programme of this Symposium might lead to the conclusion that the subject of metallography was the most important branch of microscopical research. In point of fact this is not so. Although the importance of the subject is admitted, yet the amount of attention given to it is not anything like so great as that devoted to biological researches. It is therefore probably quite true that ninety per cent. of the microscopes in use at the present time, whether in this or any other country, are in the hands of those who are working at biological subjects. Even of this class, the science of medicine will absorb the greater portion; and it is therefore unfortunate that the medical side of the subject is treated so lightly—at least, if we may judge from the programme. It is, I am afraid, only in accordance with the accustomed attitude in medical circles for little interest to be taken in pure microscopy, although in diagnostic work the importance of the microscope has never assumed a larger place.

In view of the paucity of contributions on the biological side, I shall, therefore, direct more attention to this than I should otherwise have done, and the few remarks I make will be more particularly in relation to the microscope as used for biological research.

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A consideration of the microscope resolves itself of necessity into two parts, the mechanical and the optical. From the mechanical standpoint there are two designs in general use—those referred to as the Continental and the English form of microscope. In the Continental type it has usually been customary to have what is known as the horseshoe foot, mainly, I imagine, because of its ease of construction by mechanical engineering methods; whereas the English design of microscope, which has hitherto been mainly made by hand, is of a more steady type, and the points of support are so distributed as to give more stability to the instrument in any position.

The essential parts of the instruments are a coarse adjustment, to give the body tube a quick motion in the direction of the optic axis, and a fine adjustment, which gives it a much slower motion in the same direction. The tube is adjustable in length, to enable correction to be made for varying thicknesses of cover glass, although a large number of workers appear to regard it as a ready method of obtaining greater or less magnification, with disastrous effects on the resulting image.

There is only one fixed part of a microscope which is used for biological purposes, and that is the stage. But metallographers require that the stage shall also be adjustable in the direction of the optic axis. The body tube itself should be made so that it can be closed to a length of 140 millimetres, including any objective changing device that may be on the nose-piece; and it should be possible to lengthen it to at least 200 millimetres or 250 millimetres if long-tube objectives are used.

All these adjustments are in the direction of the optic axis of the instrument. Two others are usually provided, which are at right angles to this direction—that is, a mechanical stage for actuating the object, and in certain of the best class instruments an arrangement for centering the sub-stage condenser to the axis of the objective. While there are many points which might be raised on the mechanical side, there are only one or two that I have time to mention. The main points about most microscopes appears to be that they are unstable. I have a considerable number in my own possession, but I do not think I have one, even now, which, if I centre an object on the stage with the instrument in a vertical position, still maintains its centration accurately if the instrument is put into the horizontal. The probability is, therefore, that there are few microscopes made at the present time that exactly fulfil the conditions necessary for high-class photomicrographic work, or for observational microscopic work of an exacting order. I trust, however, that an instrument exhibited at this Symposium will embody the necessary improvements to rectify this matter.

Some misapprehension appears to me to exist also as to the relative purpose of the coarse and the fine adjustments. The coarse adjustment should be sufficiently well made, and if the user is sufficiently expert, to enable him to bring into view any object, whether it is being observed with a low or a high power objective. The fine adjustment is then used for accurate focussing and for getting a conception of the object in depth. In biological work, at any rate, this is very rarely the state of affairs as carried out. In using

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an oil immersion objective, for instance, a common method is to immerse the objective and then lower it so that it all but touches the top surface of the cover glass. The objective is then raised by means of the fine adjustment until the object comes into view. While this may act fairly well with very thin cover glasses, it is a haphazard method when cover glasses of varying thicknesses are used. It should be realised that when microscope users are sufficiently educated, they will be able to tell how far they are from the actual image by the appearance of the light in the field of view, that is, if the object is illuminated with reasonable accuracy.

Mechanical stages also appear to me to need some consideration. The stages which will on actuation cause no shift of the object other than in the direction intended, or any alteration of focus, are rare. Further, those in which the screws project over the side for a considerable distance with the result that any slight jar or knock causes them to be displaced, and, it may be, actually bent, are objectionable when used under laboratory conditions.

There is, I think, much to be said for the type of stage which has either co-axial milled heads on a vertical axis, or, if inconvenient to make, milled heads which are on separate axes. This method of construction, I think, of necessity results in a much stiffer and more stable stage. There is, in fact, a general lack of stability going through nearly all parts of a microscope. But it is significant that, even so long ago as the beginning of last century, the instrument as then designed had much greater attention paid to this point. The microscope, an illustration of which I show on the screen, is to my mind an embodiment of a principle that should receive attention. So soon as English makers are in a position to consider the production of an instrument of a special type, it is my intention to have one made. In this the general principle is that all the optical parts are carried on a bar which is, in effect, an optical bench, and that this is strutted in such a way as to give stiffness to the instrument as a whole. The only effort that I am aware of that has been made in this direction is in the microscope designed by Dr. Rosenhain, particluarly for metallography, but which is adaptable for ordinary work. This instrument, to my mind, is such an improvement on any other type of stand that I am at a loss to understand why metallographers have not more generally taken it up. It might appear that I am exaggerating the importance of stability in the stand. But it should be realised that any want of centration in the optical parts, or want of alignment in the optic axes of these parts, results in more serious deterioration of the resulting microscopic image than any other single factor. The optical parts of a microscope are the objective, for obtaining the primary magnified image of the object; the ocular, for further enlarging that image and transmitting it to the eye; and the sub-stage condenser, for illuminating the object with a larger or smaller cone of light. The limitations of time will prevent me from doing more than refer very briefly to some properties of the optical parts.

It is generally assumed that magnification is the primary function of an objective. But in point of fact the main point is not magnification but resolution. By resolution is meant the power the

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objective has of separating and forming correct images of fine detail. That known as the Abbe Diffraction Theory, is the theory on which modern optical calculations are based, and it is safe to say that it was never more fully accepted and never rested on a surer basis than at the present time. There has been much discussion in this country of that theory, and probably a good deal of misconception has arisen from its inapt designation; for the term "Diffraction Theory" is perhaps somewhat unfortunate. I cannot do better than quote the late Lord Rayleigh in reference to this matter. He said: "The special theory initiated by Professor Abbe is usually called the Diffraction Theory, a nomenclature against which it is necessary to protest. Whatever may be the view taken, any theory of resolving power of optical instruments must be a diffraction theory in a certain sense, so that the name is not distinctive. Diffraction is more naturally regarded as the obstacle to fine definition, and not, as with some exponents of Professor Abbe's theory, the machinery by which good definition is brought about."

This very clearly and accurately sums up the position. The Abbe theory tells us that there are two main factors determining resolution: that is, the numerical aperture of the objective used, and the wave-length of the light. Numerical aperture is determined for us by the optician, and it is well known that, with an oil-immersion objective, a numerical aperture of 1.4 is at the present time the practical limit. Metallographers are in a somewhat stronger position, as a mono-bromide of naphthaline immersion objective was, and presumably still is, made by Zeiss, which had a numerical aperture of 1.6. This represents the absolute limit at the present time, and there is no indication that numerical aperture will be increased in this sense by present methods.

The other factor governing resolution is the wave-length of light, and in this connection it must be borne in mind that to resolve a regularly marked structure, the distance between the markings must be more than half a wave-length. Under ordinary conditions of illumination we cannot go very far in the direction of increased resolution unless we have resort to an illuminant such as a mercury vapour lamp, which is rich in blue and violet radiations. There is much room for investigation in this direction, as the ideal illuminant for microscopic work has yet to be found. But I do not know of any one that approaches so nearly to it as the one I have mentioned—the mercury vapour lamp. It suffers only from one disadvantage that I can see, and that is that the differentiation due to staining is not so clearly brought out as when ordinary light is used. But as staining is itself an artificial process, and is simply done to differentiate structures, it only means a certain amount of education to enable us to appreciate the differences, even under the light from this lamp. The only stains which it does not show quite well, or, rather, in which the colour-tint is altered, are those in which red predominates. Any other colour is shown perfectly and in reasonable gradation. The advantages of this illuminant are that it is even and uniform. It has a fairly large area, and can be used therefore for any class of work. Its intensity can be varied within considerable limits by having a resistance in series, so that the current density is altered to suit the particular

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work under observation. Further, it is possible, by interposing neutral screens, to vary the light intensity if the electrical method is inconvenient. Owing to its possessing practically no red radiations, its mean wave-length is shorter, and by using suitable screens light which is truly monochromatic, green, blue or violet, can be obtained at will. These lamps are made both in glass and quartz, but the quartz ones are preferable, because they admit of the use of heavier current, with greater luminosity; and further, they have a much longer life. I have exhibited two of these lamps, because I regard them as far in advance of any other form of light available to the microscopist at the present time, whether he is a biologist or a metallographer.

The whole subject of illumination, so far as the illuminant is concerned, needs investigation also, because there is, I think, little doubt that a modification in the intensity of the illumination of any particular object enables us to use a larger light cone than we could do under ordinary circumstances. That is, variation of the intensity is an alternative to the use of the iris diaphragm in the sub-stage of the microscope. But it is in the direction of using invisible radiations in the ultra-violet, or, it may be, radiations which are still shorter than the ultra-violet, that developments in microscopic work are, in my opinion, likely to occur.

There are two other points, which I can only refer to, but which, I trust, may be dealt with more fully in the succeeding papers. One is that, while the resolution limits are so inflexible, that does not by any means apply to mere visibility. By illuminating small particles by means of an annular cone of rays, that is, what is ordinarily known as dark ground illumination, or by illuminating them at right angles to the optic axis of the microscope—what is known as the ultra-microscopic method—particles of a very much smaller order of size can be made visible. But we cannot tell anything about their form, nor can we accurately tell their size. We are only conscious of their mere existence.

Another point to remember is that magnification is definitely limited to something like 750 diameters with microscopes under ordinary conditions, if we want to get the best optical effect. We may, as a matter of convenience, have still higher magnifications, because it is not given to everybody to appreciate fine detail unless an image is somewhat enlarged. But it must be appreciated that any increase beyond 750 or 800 diameters does not result in us seeing anything more. It simply allows us to see the object on a somewhat larger scale. We may therefore summarise as follows:—An object which is much smaller in size than the resolution limit can be rendered visible, providing the light with which it is illuminated is of sufficient intensity, and it is sufficiently different in refractivity from the medium in which it lies. To resolve a series of equi-distant points or lines in an object, their distance apart must exceed half a wave-length of light in the medium in which the object is immersed. Johnstone Stoney has shown that a pair of lines or objects can be separated when their distance apart is rather smaller than the resolution limit required for a number of points or lines in a row. But it should be borne in mind even here that the resolution limits apply if a definite standard of definition is required. An isolated object, or pair of objects, are not so well

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defined if they exceed the resolution limits as laid down for recurring structures. It cannot be too fully appreciated that illumination is the keynote of all sound microscopic work, and this applies whether the illumination is by means of visible radiation under ordinary conditions of work, or whether it is in experimental work in which the use of invisible radiations are concerned.

There is much room for research in this direction, and it is to be hoped that this is one of the points which will be seriously taken up. Apart from any question of research, the education of the user is perhaps of vital importance. It is little use for opticians to make great efforts to turn out a satisfactory instrument if the user is incapable of taking advantage of the quality of the optical or other parts. I trust, therefore, that this Symposium will give an impetus in this direction, and that it will help microscope users to realise how much remains to be done.

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ADDRESS BY SIR HERBERT JACKSON, K.B.E., F.R.S.

At this stage **Sir Herbert Jackson** delivered an Address, which is printed on page 213 of this Report, owing to an unavoidable delay in preparing it for publication.

Professor F. J. Cheshire, C.B.E., President of the Optical Society, read a paper on "The Mechanical Design of Microscopes."

THE MECHANICAL DESIGN OF MICROSCOPES.

By Professor F. J. Cheshire, C.B.E.,
President of the Optical Society.

The optical industry in this country, as the result of war experience, has been specially recognised by the Government as a key industry, which, in the national interests, therefore, must be encouraged and preserved.

Now the microscope, whether considered from the point of view of the great and increasing demand which it makes upon the highest technical knowledge and skill of the optician and the mechanician, the importance of the work which it is called upon to do, or the great demand for it, stands forth as the most important of all optical instruments. It is thus the keystone of the arch of a key industry. The optical industries of any country which is producing microscopes for which there is a world's demand must be in a healthy and thriving condition. Conversely, any country which fails to produce a microscope to meet the world's demands is very unlikely to have the reputation for producing, on a commercial scale at at any rate, important optical instruments of any kind. The production of the microscope may therefore be accepted as the touchstone of national success in optical activities generally. The importance of this point must be insisted upon—when England can produce microscopes in large numbers for the world's markets, the success of her industries will be assured. Until it does so, that success cannot be accepted as assured.

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The development of a mechanical invention which is ultimately required to meet a big demand, usually follows upon well defined lines. At the beginning, when the demand is small, the labour of highly skilled craftsmen is necessary and sufficient for its production, but later, when the demand has increased, it is found that for efficient production the skilled craftsman is no longer sufficient, but special machinery must be put down to replace him. In other words, artistic production is followed by machine production.

As an illustration of production in the artistic period, I cannot do better than tell you a story that was told to me some years ago by the late Dr. Czapski. Dr. Czapski upon one occasion visited Hartnack, the famous maker of microscope water-immersion objectives. He found him sitting on a stool in front of a window, busily engaged assembling the systems of his objectives with the aid of a microscope and a test-object. On the table by his side were a number of grooved sticks, each filled with a number of a particular lens wanted in a certain objective combination. Hartnack, with his great knowledge and skill, was able to look at a critical object and decide from its appearance what lens in a given combination was likely to be responsible for the observed defects. He would then try another and slightly different one in its place. In this way he would try combination after combination, until a satisfactory result was obtained. Occasionally by a fortuitous accident he would obtain an objective much superior in its performance to the general run. These were carefully put on one side, and although Hartnack charged a uniform price for all his objectives, he was very careful to allow none but serious workers to obtain possession of the best quality lenses. Now Abbe realised that this method of production, making such great demands upon unique knowledge and skill, could not possibly meet the growing world's demand for microscope objectives, and therefore that the highly skilled, technical artist must be dispensed with and replaced by mechanical processes capable of producing to a high order of accuracy predetermined elements. This was done, and that success which is now a matter of history, achieved. Some time ago I was discussing this subject with Sir Howard Grubb, and he gave me a remarkable instance from his own experience. He told me that before the war he employed a skilled man to rough out certain lenses by hand at the rate of about a dozen per week. When the war broke out it was realised that something must be done to expedite production, and Sir Howard Grubb invented a special machine, attended by a girl, to perform the necessary operation. The result was that the girl and the machine turned out more than a thousand of these lenses per week.

It follows from what has been said that the microscope must meet not only the demands of the user, it must meet also those of the manufacturer. I suggest, therefore, that a well designed commercial microscope may be defined as one that can be made both accurately and cheaply, and that secures in its use "the greatest happiness of the greatest number." First, it must be a commercial article, one made in great numbers to compete in the markets of the world. Secondly, it must be made accurately and cheaply. These requirements necessitate on the part of the manufacturer specialisation, standardisation, production by repetition machinery

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of the most modern types, attended by unskilled labour; the whole of these activities being directed by the highest technical knowledge and skill. Thirdly, a well designed microscope must confer the greatest happiness upon the greatest number of its users. In other words, it must meet to the fullest possible extent, the needs and demands of its users. But these demands are constantly changing and increasing. Demands resulting from war experience, for example, are already of a formidable nature, and are certain to become greater. One fundamental difficulty in design must be noted. A good design having been evolved to meet existing requirements, there is always a strong temptation to meet new requirements by a modification of the old design. In any particular case this may or may not be satisfactory, but one is often inclined to wonder whether this subservience to tradition has not resulted in the perpetuation of designs which, however good they may have been at one time, are now ill-adapted to meet more exacting requirements. A thorough overhaul of the design of the microscope by thoroughly skilled mechanicians, without reference to old and traditional designs, might lead to startling and valuable results. This is a point of great importance to the trade. So long as a manufacturer confines himself to the production of well-known designs, he must of necessity meet with keen competition. Should he, however, be successful in introducing new and valuable features, his chance of success is very greatly increased. This danger of too close an observance of traditional designs is unfortunately enhanced by mass production, because when a manufacturer has laid down expensive plant to produce a given design, it often pays him—or he thinks it does—to buy up patents for improvements upon it, and throw them into the waste-paper basket.

Again, in the elaboration of a standard design we all agree that the faddist must not be considered—the greatest happiness of the greatest number must be sought for. Here, again, the matter is not so easy in practice. We are now told that the bullet which eventually brought down the Zeppelin so ignominiously was, in the first case, refused as the suggestion of a crank. Many valuable suggestions for the improvement of the microscope must also have been turned down for the same reason in the past.

Time, unfortunately, does not permit of any consideration or criticism of the design of the details of the microscope, but there is one matter of some importance to which I should like to draw your attention. In the early days of the microscope the illuminating apparatus was of the simplest kind, generally nothing more than the sky or a common lamp, the light from which was thrown upon the object by a simple mirror. Modern work, however, demands a well-corrected condenser of large aperture—or it may be a dark-ground illuminator—working in conjunction with a small and intense light source accurately adjusted in the axis of the complete illuminating and observing systems. Now this adjustment of the light source is tiresome in the case of an expert, and difficult in the case of a tyro, and, when made, a touch of the mirror, or a slight accidental displacement of the microscope or the lamp, necessitates the work being done again. This difficulty could be largely removed by the simple expedient of resting the microscope and the lamp on geometrical bearings of the three-radiating groove type. In the

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case of the microscope these grooves could be cut in the foot of the instrument to rest upon and engage with three studs on the table. This arrangement would be simple and cheap, and would have the further advantage that it would not in any way interfere with the use of the microscope in the usual way—the grooves when not in use would not scratch the table top. In this simple way the placing of the lamp and the microscope in a fixed position with respect to one another, would be secured. It would then only be necessary to fix the mirror, as has been suggested by Mr. J. E. Barnard, and the microscopist would, in a few seconds, be able to ensure that a beam of light was being thrown accurately along the axis of his microscope, a necessary condition, for example, of the efficient use of the dark ground illuminator in bacteriological work.

I have not been able to say much, ladies and gentlemen: the time has been too short, but I hope that I have been able to say something which will assist you to realise the national and far-reaching importance of the subject with which we are concerned at this Symposium to-day.

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Mr. F. Martin Duncan, President of the Photomicrographic Society, then gave a résumé of his paper, "Some Notes on the History and Design of Photomicrographic Apparatus."

SOME NOTES ON THE HISTORY AND DESIGN OF PHOTOMICROGRAPHIC APPARATUS.

By F. Martin Duncan, F.R.M.S., F.R.P.S., F.Z.S.
President of the Photomicrographic Society.

No survey of the present position of microscopy would be complete without a reference to the very important part which photomicrography plays as a means of accurately recording the various objects which are submitted to microscopic examination. To the investigator in bacteriology, biology, and metallography, a photomicrographic apparatus is to-day an essential part of his microscopic outfit, and therefore the consideration of the design of such apparatus has become a matter of prime importance.

Scientific workers were quick to realise the value of photography as a means of obtaining an unbiased graphic record of their observations, and it was only the limitations and technical difficulties of the early processes that prevented its wider use. From the time of its first discovery there have been microscopists who have employed photography in preference to the pencil. Thus in 1845 Doune and Foucault illustrated their "Atlas of Microscopic Anatomy" by etchings from photomicrographs taken on Daguerreotype plates, while as early as 1835 Fox-Talbot had obtained images of objects in the solar microscope by means of his recently discovered process. It would be out of place here to enter into a description of the early pioneers of photography, intensely interesting though the subject be, but in passing one cannot help feeling proud of the fact that the discovery of photography was due to British and French scientists alone, and that the first to apply it successfully to the recording of microscopic objects were Fox-Talbot in England, Daguerre in France, and Draper in America. And since those first days of the history of photomicrography, it has been in France, in Great Britain, and in America that the greatest experts, the most notable advances and inventions, and the most perfect apparatus for photomicrography have been produced.*

Naturally the apparatus used in the early stages of the application of photography to microscopy was of a somewhat crude character. The earliest cameras were little more than light-tight boxes, while many of the pioneers dispensed with any form of camera at all, the

* For a short account and early bibliography see an article entitled "Chapters in Photomicrography," which I contributed to the *British Journal Photographic Almanac* for 1903, pp. 691-725.

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eye-piece end of the microscope being inserted through a circular hole in the wall of the dark-room, and the Daguerreotype plate, or the wet collodion plate placed upon a board in the dark-room, on which the image formed by the microscope had previously been focussed. Considerable difficulties had to be overcome in obtaining the correct adjustment that would yield a sharp, crisp image, owing to the, at that time, imperfect corrections of microscope objectives; but gradually from such crude beginnings the practice of photomicrography has attained to its present high standard of technique. That the rapid improvement and high standard of perfection to which microscope objectives, eye-pieces, and substage condensers have reached are largely due to the investigations and labours of Abbe, Schott, and Zeiss, all microscopists will readily admit; but that is about all, though admittedly it is a very important contribution, that can honestly be claimed by Germany as her share towards the perfection of photomicrography.

I know that opinions are very sharply divided on the subject of the microscope stand as made by British and German manufacturers, and I feel that much of the criticism that has been levelled at the British manufacturers is grossly unfair and inaccurate, because in nine cases out of ten the would-be critic is already prejudiced in favour of the German, has not a thorough technical knowledge or experience, and frequently has never used a really first-class British stand. I am quite ready to admit that the British maker has turned out some very poor models, but so has the German; but because the Britisher has produced some cheap models of poor quality, surely that is no reason for damning at sight everything he produces. You are not going to encourage home enterprise or industry by such methods. I have now used the microscope practically daily for over thirty years in my biological investigations, and during that time models by all the leading British and Continental manufacturers have passed through my hands, and have been, I hope and believe, honestly, critically, and impartially tested. Out of that long experience I am bound to say that for comfort in working, rigidity, and perfection in design and workmanship, I have yet to see the German or Continental model that will touch the very best productions of our leading British manufacturers. In no branch of microscopy is the superiority of the first-class British microscope stand more readily demonstrated and realised than in critical high-power photomicrography, for to produce the best results, rigidity, whether in the vertical or horizontal position of the microscope body, and ease of manipulation of the mechanism of the substage and the top or object stage are factors of vital importance—factors which are not present in the horseshoe foot, or the finicky studs and knobs provided for the adjustment of substage and substage-condenser, and mechanical stage, in the German models. Even the large Zeiss model specially designed by that firm for photomicrography, though of good workmanship, suffers from these inherent defects of the Continental model, its substage mechanism being very cramped, and the mechanical stage provided with wretchedly small pinion heads.

The microscope stand intended for critical photomicrography and original research should have a solidly cast broad tripod foot, such as is present in the large research model of Swift, the R.M.S. model

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of Baker, or the Royal and Van Heurck models of Watson. The focussing of the substage condenser should be by a stout pinion of such a length that the hand does not have to grope for it beneath the stage, and should be provided with a good milled head. Fairly stout pinions and milled heads should also be provided for controlling the vertical and transverse movements of the mechanical stage, while the body-tube should be of large diameter to admit the use of low-power objectives required when photographing comparatively large fields.

Between the years 1889 and 1899, Messrs. Swift and Messrs. Baker produced two very fine photomicrographic cameras that might well to-day rank as standard models for critical high-power work. That made by Messrs. Swift incorporated designs suggested by Mr. Andrew Pringle, and that by Messrs. Baker the ideas of the late Mr. C. Lees Curties—both experienced microscopists and photomicrographers. The essential features of each outfit are very similar, and consist of (1) a long solid baseboard forming a rigid foundation on which the whole apparatus is built; (2) a substantial square-bellows camera travelling on a wide base and capable of considerable extension; and (3) a substantial turntable for the support of the microscope condensers and illuminant. On account of the wide, solid base on which the square-bellows camera travelled, the camera could be extended to its fullest degree and used in that position without fear of vibration during long exposures. With such apparatus the formidable task of obtaining sharp negatives at a magnification of upward of two thousand diameters linear, could be accomplished with certainty, and, given the necessary technical knowledge, celerity and ease. It is no light task to be called upon to produce large numbers of photomicrographic negatives at such high magnifications, when the work has to be carried out in a house past which heavy street traffic is continually travelling, yet such formed a part of my duties during the terrible years of the war, and was made possible only by the use of apparatus of the design I have just described. Before the work was placed in my hands, attempts had been made to carry it out with photomicrographic apparatus mounted on iron rods, the typical German design; and therefore, of course, supposed to be vastly superior to anything British. The failure was due to no want of skill on the part of the users of the apparatus, but to its inherent faulty design, for it is obvious that vibration will be more readily conducted and its amplitude increased along the rods than through a solid base. Both from long pre-war experience and from the result obtained in that part of my war work just described, I feel that I am fully justified in stating that the right design for photomicrographic apparatus intended for critical high-power work is on the lines of the Pringle-Lees Curties models, or the more recent designs of Singer made by Messrs. Watson and Sons, and of Barnard, made by Messrs. Baker.

It frequently is necessary to take photomicrographs with the microscope in the vertical position, and here again to employ a camera clamped to an upright iron rod is asking for trouble, to say the least, yet that is the design dear to the heart of the German manufacturer. Many years ago now, Messrs. Watson and Sons placed on the market a vertical model made to the design of the veteran microscopist, the

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late Dr. Van Heurck. The apparatus consists of a vertical box-form camera supported on four stout square legs, between which, and immediately beneath the camera, the microscope is placed. The whole is very rigid, and we all know the magnificent work Dr. Van Heurck and others produced with it. The chief objection, and, when considered on optical grounds, to my mind not a very real one, is that it precludes the employment of extended camera lengths. But ten inches from the eye lens of the eye-piece to the focussing screen of the camera is, I believe, the ideal extension for critical work with modern objectives. In the *Journal of the Royal Microscopical Society* for 1916, pages 258-9, I have figured and described a simple home-made vertical stand to carry microscope and camera, and although there shown as used for stereo-photomicrography, I have since used it successfully for high-power work with the monocular microscope with magnifications up to two thousand diameters.

A vertical apparatus of good, rigid design is of such importance for a great deal of microscopical research work that is being carried out to-day, that it is a matter deserving the immediate and serious consideration of our British manufacturers.

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Dr. Charles Singer presented the following paper on "The Earliest Steps in the Invention of the Microscope." The paper was taken as read.

THE EARLIEST STEPS IN THE INVENTION OF THE MICROSCOPE.

By Charles Singer, M.A., M.D.Oxford, F.R.C.P.Lond., F.S.A.

The microscopes and the microscopic work of the classical observers, Leeuwenhoek, Malpighi, Hooke, and Kircher, have been frequently described and figured. These descriptions are readily accessible, and I shall therefore confine myself to the earliest stages in the discovery of the microscope, which is, of course, intimately connected with the invention of the telescope. About these early stages vague statements are often made, but the actual data do not seem to have been put together.

(1) *Euclid* (third century, B.C.), in his *Optics*, considered that light passed in straight lines, and regarded an object seen as formed by a cone with its base at the object and the apex at the eye. The Euclidian origin of this work is disputed by some, who hold that is is by Theon of Alexandria, who lived in the fourth century, A.D., and was perhaps the father of Hypatia. The most recent edition is by G. Ovio, *L'Ottica di Euclide*, Milan, 1918.

(2) *Ptolemy* (died about 155 A.D.), in his *Optics*, began the study of refraction, and applied the experimental method to this subject. He showed that luminous rays, in passing from one medium to another are deflected, and he attempted to measure the deflection. This work of Ptolemy was written in Greek, and has been lost. It was translated from Greek into Arabic, and, in the twelfth century, from Arabic into Latin. Only the Latin version survives, and its attribution to Ptolemy is doubtful. The best edition is by G. Govi, Turin.

(3) *Alhazen* (Abu Ali Al-Hazan Ibn Alhasan, 965-1038), was an Arab of Basra, who abstracted the work of the older Greek optical writers. He devoted much space and skill to the development of the effects of curved mirrors. He had a fairly clear notion of the nature of refraction, and improved the apparatus of Ptolemy for measuring the angle of refraction in different media. He had

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ideas on the structure of the eye that were an improvement on those of his predecessors, but he had little knowledge of lenses, except in connection with that organ. He does, however, refer to the magnifying power of segments of a glass sphere. He considered that vision resulted from rays coming to the eye from the object, and opposed the view, which held the field till the seventeenth century and later, that explained vision as a result of something emanating from the eye. There are editions of Alhazen's work printed in the sixteenth century. These represent a translation into Latin by an unknown writer of the late twelfth or early thirteenth century (*see* 4).

(4) *Witelo* (first half of the thirteenth century) was a Pole, who studied in great detail the work of Alhazen. His own work grew out of this, and is perhaps an improvement on it. Thus he drew up a table of refractions for the three media—air, water, and glass—from which it could be seen that the angle of refraction did not vary according to the angle of incidence. It is doubtful, however, to what extent these tables were original or the results of direct observation. The works of Alhazen and of Witelo were printed together by F. Risner at Bale, 1572. An interesting account of Witelo, together with a reprint of his *Perspectiva* from the MSS. has been recently set forth by Clemens Bauemker in his *Beitrage zur Geschichte der Philosophie des Mittelalters*, Munich, 1908.

(5) *Roger Bacon* (1214-1294) accomplished real advances in the knowledge of optics. His work was based primarily on Latin translations of Arabian writers, and especially on Witelo's version of Alhazen. He is distinguished from his predecessors, however, by his clear conception of the value of experiment, and by the evidence in his works that, having made a serious and continuous effort to discover the laws of the refraction and reflection, he sought to apply his knowledge to the improvement of the power of vision. In this he is a real pioneer, and is in the truest sense the father of microscopy.

But it is easy to exaggerate the claims of Bacon, and the wildest statements are often made about his discoveries. It is a fact that there is no evidence that he ever made a telescope nor any microscope, save a simple one. But he had a clear, though not wholly accurate idea of the nature and properties of lenses, and, groping with the instinct of genius, he did vaguely foresee both telescope and microscope. The following passages will serve to indicate the stage he had reached in optical knowledge. I have purposely selected passages containing some errors. It will be observed that in the first of these passages Bacon refers to and figures the *object* as though it were itself in the denser medium of which the lens is composed. In doing this he is confusing the optical action of a lens with that of a liquid in which an object is immersed. The optical results of immersion in a liquid had been investigated by his predecessors, and were perhaps familiar to Aristotle.

" If anyone examines letters and other minute objects through the medium of crystal or glass or other transparent substance, if it be shaped like the lesser segment of a sphere, with the convex side towards the eye, and the eye being in the air, he will see the

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letters far better, and they will seem larger to him. For, according to Canon 5 (*see* Fig. 1) concerning a spherical medium beneath which the object is placed, the centre being beyond the object, the convexity being towards the eye, all causes agree to increase the size, for the angle in which it is seen is greater, the image is greater, and the position of the image is nearer, because the object is between the eye and the centre. For this reason such an instrument is useful to old persons and to those with weak eyes. For they can see any letter, however small, if magnified enough. But if a larger segment of a sphere be employed, then, according to Canon 6

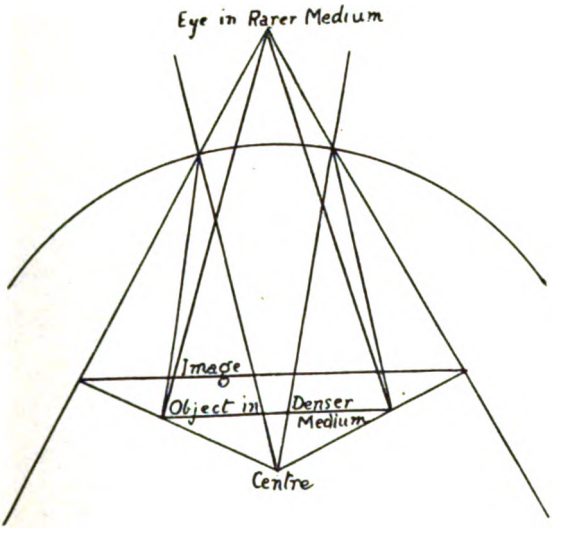

FIG. 1

(Fig. 2), the size of the angle is increased, and also the size of the image, but propinquity is lost because the position of the image is beyond the object, the reason being that the centre of the sphere is between the eye and the object seen. Therefore such an instrument is not of so much use as the smaller portion of a sphere."

"Objects are greater when the vision is refracted; for it easily appears by the above-mentioned canons that very large objects may seem to be very small and conversely, and those at a great distance away may seem very near and conversely. For we can so form glasses and so arrange them with regard to our sight and to objects that the rays are refracted and deflected to any place we wish, so that we see the object near at hand or far away beneath whatever angle we desire. And so we can read the smallest letters or count grains of sand or dust from an incredible distance, owing to the magnitude of the angle beneath which we see them, while we can scarcely see the largest objects close at hand, owing to the smallness of the angle beneath which we view them; for distance does not affect this kind of vision save *per accidens*, but the size of the angle

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(does so affect it). So a boy can appear a giant, a man seem a mountain, and in any size of angle whatever, just as we can see a man under so large an angle like a mountain and as near as we desire. So a small army might seem very large, and though far away appear near, and conversely: so too we could make sun, moon, and stars apparently descend here below, and similarly appear above the heads of our enemies, and many other similar marvels could be brought to pass, so that the ignorant mortal mind could not endure the truth." (*Opus Majus*, Part V).

"And what is causally manifest with regard to double refraction we can verify in many ways by the results of experiment. For if anyone holds a crystal ball or a round urinal flask filled with water in the strong rays of the sun, standing by a window in face of the

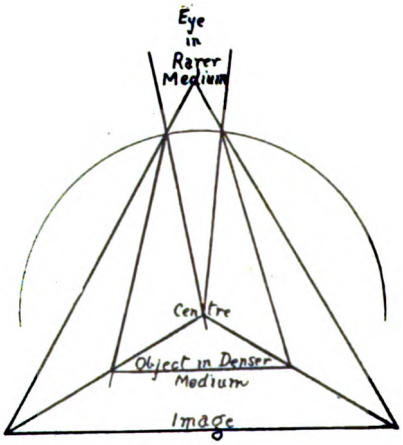

FIG 2.

rays, he will find a point in the air between himself and the flask at which point, if any easily combustible substance is placed, it will catch fire and burn, which would be impossible unless we suppose a double refraction. For a ray of the sun coming from a point in the sun through the centre of the flask is not refracted, because it falls perpendicularly on flask, water, and air, passing through the centre of each (Fig. 3). . . . But all the (other) rays which are given forth at the same point in the sun from which this perpendicular ray comes are necessarily refracted on the body of the flask, because they fall at oblique angles, and since the flask is denser than air, the refraction passes between the straight path and the perpendicular drawn from the point of refraction to the centre of the flask. And when it passes out again into the air, then, since it comes upon a less dense body, the straight path passes between the refraction and the perpendicular drawn from the point of refraction, so that the refracted ray may fall upon the first perpendicular which comes without refraction from the sun. And since an infinite number of rays are given off from the same

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point of the sun, and one only falls perpendicularly on the flask, all the others are refracted and meet at one point on the perpendicular ray which is given off along with them from the sun, and this point is the point of combustion, because on it are collected an infinite number of rays, and the concentration of light causes combustion. But this concentration would not take place except by double refraction, as shown in the diagram." (*Opus Majus*, Part VII).

"Glasses (*perspicua*) can be so constructed that objects at a very great distance appear to be quite close at hand, and conversely. Thus we read the smallest letters from an incredible distance, number objects, however small, and make the stars appear as near as we wish. . . . Also objects can be made to appear so that the

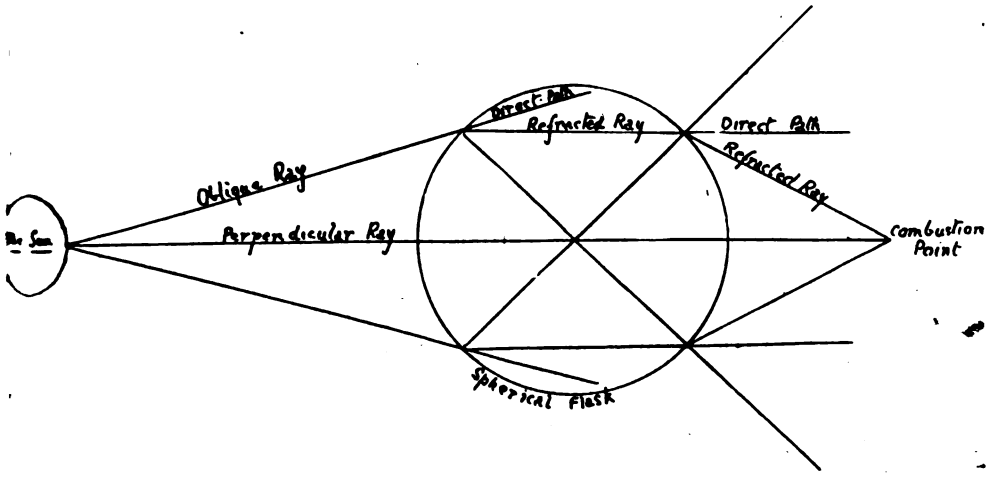

FIG. 3.

greatest seems the least, and conversely; what are high appear low and short, and conversely; and what is hidden appears manifest. . .

But among the more subtle powers of construction is this of directing and concentrating rays by means of (instruments of) different forms and reflections at any distance we wish, where whatever is subjected to them is burned. . . . But greater than any such design or purpose is that the heavens might be portrayed in all their length and breadth on a corporeal figure moving with their diurnal motion, and this would be worth a whole kingdom to a wise man. Let this, then, be sufficient as an example, although an infinite number of other marvels could be set forth." (*De Secretis Operibus Artis et Naturae.*)

It is a remarkable thing that no complete edition of the works of Roger Bacon has ever been prepared, nor any important work by him translated into English. The above passages I have translated from J. H. Bridges, *The Opus Majus of Roger Bacon*, Oxford, 1897, and J. S. Brewer, *Fratris Roger Bacon opera quaedam hactenus inedita*, London, 1859.

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(5) *John Peckham* (died 1292), Archbishop of Canterbury, was the author of a work on optics entitled *Perspectiva communis*. His views were very similar to, and, perhaps, taken from, Bacon. He is important only as having drawn wide attention to optical principles. His work exists in a number of manuscripts, and has often been printed. The first edition is dated from Milan, 1482.

(6) The names of Salvino d'Amarto degli Amarti of Florence and Alessandro de Spina of Pisa (both circa 1300) have become associated with the special application of lenses for use as spectacles. Lenses, as we have seen, were known to Roger Bacon, who suggested also their use in aiding vision. D'Amarto and Spina applied the principle thus suggested. From about 1300 onward convex lenses for use as spectacles were well known.

The question of the invention of spectacles has been frequently discussed. One of the latest writers who has traversed this field is V. Rocchi, *Appunti di storia critica del microscopio*, in the *Revista di Storia critica delle Scienze Mediche e Naturali*, January, 1913.

(7) *Leonardo da Vinci* (1452-1519) had sounder ideas than any of his predecessors on the structure of the eye, on binocular vision, on refraction and diffraction. He developed a practical *camera obscura*, and gives a hint of a "glass to see the moon enlarged." His work, though original and valuable, remained inaccessible for nearly four centuries, and had no influence on his contemporaries.

Leonardo left his scientific remains in a state of confusion, and they have suffered much by time and misuse. It is impossible to give a bibliography here, but his optical results are summarised by E. Solmi, *Leonardo da Vinci e il metodo sperimentale nelle ricerche fisiche*, in the *Atti e memorie della R. Accademia Virgiliano di Mantova*, Mantua, 1905, and by O. Werner, *Zur Physik Leonardo da Vincis*, Berlin, 1911.

(8) *Girolamo Fracastoro* (1478?-1553) was a suggestive writer who devoted considerable space to a rather confused account of refraction. In the course of this discussion he has the following passage:—"(Not only the character but) also the position of the medium affects the appearance of the objects seen, as may be observed with spectacle lenses (*in specillis ocularibus*). For if the lens be placed midway between eye and object, it appears much larger than if the lens is made to approach the object or the eye. (*Homocentrica* II, 8). . . . Glasses (*specilla ocularia*) may be arranged of such density that if anyone looks through them at the moon or at any star they appear near and hardly higher than the steeples. (*Homocentrica*, III, 23)." It is possible that he was here contemplating a bilenticular apparatus. The *Homocentrica* in which these passages occur was first printed at Venice in 1538. The scientific value of this work is discussed by the present writer in an article in the *Annals of Medical History*, Vol. I, p. 1, New York, 1917.

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(8) *Francesco Maurolico* (1494-1575) was perhaps the first after Roger Bacon to attempt a mathematical analysis of the optics of the lens. He is thus the predecessor of Kepler. His work, *Photismi de lumine et umbra*, was printed at Venice in 1575.

(9) *Leonard Digges* (died 1571?) was the first to whom can be definitely attributed the construction of a bilenticular system. The evidence for this statement rests on the following passage in a work by his son, Thomas Digges (died 1595):—

"Marueylouse are the conclusions that may be perfourmed by glasses concaue and conuex of circulare and parabolicall fourmes, using for multiplication of beames sometime the ayde of glasses transparent, which by fraction should unite or dissipate the images or figures presented by the reflection of other. By these kinds of glasses or rather frames of them, placed in due angles, ye may not only set out the proportion of an whole region, you represent before your eye the lively image of euery towne, village, etc., and that in as little or great space or place as ye will prescribe, but also augment and dilate any parcell thereof, so that whereas at the firste apparance an whole towne shall present it selfe so small and compacte together that ye shall not discerne any difference of streates, ye may by applycation of glasses in due proportion cause any peculiare house or roume thereof dilate, and shew it selfe in as ample fourme as the whole towne first appeared, so that ye shall discerne any trifle or reade any letter lying there open, especially if the sonne beames may come unto it, as playnly as if you wer corporally present, although it be distante from you as farre as eye can discrye. But of these conclusions I minde not here more to intreate, hauing at large in a volume by it selfe opened the miraculous effectes of perspective glasses." Digges's system appears to have been combined in some manner with a *camera obscura*. Unfortunately, his further description of it was never published. The work of Thomas Digges in which this passage occurs is entitled *A Geometrical Practise named Pantometria*, and was printed in London in 1571.

(10) *Gianbattista della Porta* (1540-1615) is the first to whom can be attributed the actual combination of lenses in the form of a microscope. This statement rests on the evidence of the following passages in his *Magia naturalis*:—"Concave lenses enable one to see far off more clearly, while convex ones make near objects more discernible." He was apparently myopic, for he goes on to say that "with a concave lens you see things afar smaller but plainer, with a convex lens you see them larger but less distinct. If, however, you know how to combine the two sorts properly, you will see near and far both large and clear." In later years, when the microscope became a recognised instrument, much larger claims were made by and for Porta, but there is no real evidence that he made any effective practical application of his idea. The *Magia naturalis* was first printed at Naples in 1558, but the passages in question do not occur in it, nor in any edition of the work that appeared before that of 1588.

(11) *Zacharias*, son of Jan, and known as Jansen (1580-16?), of Middelburg, is usually regarded as the first who actually constructed a microscope. His first attempt was the result of an

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accident. It appears that while still a lad and at work in the shop of his father, who was a spectacle maker, he happened to place two lenses in a tube and found that they acted as a microscope or telescope. Effective instruments were constructed by him in the first decade of the seventeenth century. The evidence that Jansen was really the first constructor of these bilenticular instruments rests on the testimony of Willem Boreel (1591-1668), the Dutch Ambassador to France. Boreel's evidence is given in a letter by him to Pierre Borel (1620-1671), which runs as follows:—

"I am a native of Middelburg, the capital of Zeeland, and close to the house where I was born . . . there lived in the year 1591 a certain spectacle maker, Hans by name. His wife, Maria, had a son Zacharias, whom I knew very well, because as a neighbour and from a tender age I constantly went in and out playing with him. This Hans, or Johannes, with his son Zacharias, as I have often heard, were the first to invent microscopes, which they presented to Prince Maurice, the governor and supreme commander of the united Dutch forces, and were rewarded with some honorarium. Similarly, they afterwards offered a microscope to the Austrian Archduke Albert, supreme governor of Holland. When I was Ambassador to England in the year 1619, the Dutchman Cornelius Drebbel of Alkomar, a man familiar with many secrets of nature, who was serving there as mathematician to King James, and was well known to me, showed me that very instrument which the Archduke had presented as a gift to Drebbel, namely, the microscope of Zacharias himself. Nor was it (as they are now seen) with a short tube, but nearly two and a-half feet long, and the tube was of gilded brass, two fingers breadth in diameter, and supported on three dolphins formed also of brass. At its base was an ebony disc, containing shreds or some minute objects which we inspected from above, and their forms were so magnified as to seem almost miraculous." This passage is contained in a work by Pierre Borel, *De vero telescopii inventore cum brevi omnium conspiciliorum historia*, The Hague, 1655.

(12) *Jan Lippershey* of Wessel (flourished 1608) is another candidate for the same honours as Zacharias. In October, 1608, a man named Lippershey applied at the Hague for a monopoly in the making of a bilenticular apparatus for examining objects at a distance. Even at that date, however, it appears from the evidence that such instruments were already known. The story of Lippershey's discovery is suspiciously like that told of Zacharias. The application and findings of the committee that sat on it were still in existence in the early part of the nineteenth century, and were published by J. H. van Swinden. *See* S. Moll, *Journal of the Royal Institution*, Vol. 1, 1831.

(13) *Jacob Andrianzoon*, otherwise *James Metius* of Alkmaar, was a younger brother of a distinguished geometrician. Of him Descartes, in his *Dioptrique*, published in 1637, writes as follows:— "It is about 30 years since one named Jacques Metius, an unlearned man, but one who loved to make mirrors and burning glasses, having by him glasses of various shape, thought of looking through two of them, of which one was convex, and the other concave, and he

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luckily put them in the ends of a tube, and thus the first telescopes were made." Metius also applied for a patent, and a copy of his application has survived among the MSS. of Christion Huygens (1629-1695).

(14) *Galileo* (1564-1642) was the effective discoverer of the microscope, a discovery which, as in the other cases, was bound up with that of the telescope. The event may be referred to the early part of 1609, and the story may be told in a translation of his own words:—

"About ten months ago," he says, "a rumour reached me of an ocular instrument made by a certain Dutchman by means of which an object could be made to appear distinct and near to an eye that looked through it, although it was really far away. . . . And so I considered the desirability of investigating the method, and I reflected on the means by which I might come to the invention of a similar instrument. A little later, making use of the doctrine of refractions, I first prepared a leaden tube, at the ends of which were placed two lenses, each of them flat on one side, and as to the other side I fashioned one concave and the other convex. Then, moving the eye to the concave one, I saw the objects fairly large and nearer, for they appeared three times nearer and nine times larger than when they were observed by the naked eye. Soon after I made another more exactly, representing objects more than sixty times larger. At length, sparing no labour and no expense, I got to the point that I could construct an excellent instrument so that things seen through it appeared almost a thousand times greater and more than thirty-fold nearer than if observed by the naked eye." (*Siderius Nuncius*, Venice, 1610).

In another work he says: "Some would tell me that it is of no little help in the discovery and resolution of a problem to be first of all in some way aware of the true conclusion and certain of not being in search of the impossible, and that therefore the knowledge and the certainty that the microscope had indeed been invented had been of such help to me that perchance without that I should not have discovered it. To this I reply that the help rendered me by the knowledge did indeed stimulate me to apply myself to the notion, and it may be that without this I should never have thought of it. Beyond this I do not believe that knowledge to have facilitated the invention. But, after all, the solution of a problem, thought out and defined, is a work of some skill, and we are not certain that the Dutchman, the first inventor of the telescope, was not a simple maker of ordinary lenses who, casually arranging glasses of various sorts, happened to look through the combination of a convex and a concave one placed at various distances from the eye and in this way observed the effect that followed thereon. But I, moved by the knowledge given, discovered it by a process of reasoning." (*Il saggiatore*, Rome, 1623.)

(15) Galileo's account of the path of light in the bilenticular system is unsatisfactory, but was improved by Kepler in his *Dioptrice* (Cologne, 1611), who at the same time suggested that form of microscope consisting of two convex lenses which has developed as our modern instrument.

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Professor A. E. Conrady contributed some "Notes on Microscopical Optics," which were communicated by Professor Alfred W. Porter, F.R.S.

NOTES ON MICROSCOPICAL OPTICS.

By A. E. Conrady.

It is manifestly impossible to give an exhaustive treatise on microscopical optics in a short paper, but a brief indication of what has been done and what is likely to be accomplished in the near future may be acceptable.

The resolving and defining power of the microscope depends primarily on the high correction of spherical aberration in cones of rays of very large angular aperture. The first approximation methods which are useful in arriving at preliminary designs of telescope objectives will only give rough indications of the required forms of components even in the lower powers of microscope objectives, and they are quite useless in the case of the higher powers.

Exact trigonometrical ray-tracing must therefore form the foundation of the designer's work. It is not, however, desirable to depend entirely upon this method, for the real desideratum in every lens system is that all the light from an object-point should reach the image point along paths of the same optical length, and according to the classical limit recommended by the late Lord Rayleigh, this equality of optical paths should not be departed from to a greater extent than $\frac{1}{4}$ wave-length, say five one-millionth of an inch. It used to be thought by practical opticians that this represented a perfectly absurd and unattainable degree of perfection, but I showed long ago (Monthly Notices R.A.S., April, 1905), that so far is this from being true that the Rayleigh limit really represents a far more generous allowance, in the ratio of about 4 to 1, than the union of the geometrical rays within a "circle of confusion" equal to the resolving power of an objective, which latter condition was looked upon as practicable. Quite recently the fulfilment of the Rayleigh condition in good telescope and microscope objectives has been put to the direct experimental proof by that valuable innovation: the Hilger Lens-Interferometer. In the paper quoted above I gave a trigonometrically exact method of *determining* the phase-relation in which rays arrive at a focus. I had used the method for about 10 years at the time of its publication, and all my designs of microscope objectives are based on its use: but up to the time when I began lecturing at the Imperial College I was probably the only designer who took advantage of this method, which is not only the soundest from the theoretical point of view, but also by far the easiest and quickest. As it gives the exact amount of spherical

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aberration arising at each surface in the absolute measure of wave-lengths, it also enables a designer to avoid the unnecessary piling up of huge aberrations such as are met with in the lens systems designed by purely geometrical ray-tracing.

Recently (Monthly Notices, June, 1919), I have rounded off this earlier work by determining the complete light-distribution in the "spurious disc" which results when residuals of aberration are present, so that the designer using the optical path method can now state definitely to what extent the image points obtained with a given system fall short of the full brightness and sharpness which would result in a theoretically perfect instrument.

The chromatic aberration of microscopic objectives is also best and most conveniently determined in terms of differences of optical paths (Monthly Notices, January and March, 1904). By applying the simple formulae to both marginal and paraxial rays, a reliable measure of the higher chromatic aberrations, the so-called spherical variation of chromatic correction, is obtained, and this can then, by suitable alterations of lens curvatures, etc., be kept within those narrow limits which distinguish "semi-apochromatic" objectives from earlier types in which this variation frequently reached very serious amounts.

A microscope objective perfectly free from spherical and chromatic aberration may yet be absolutely useless for practical purposes on account of such amounts of coma in the images of extra-axial object points that sharp definition is limited to an almost infinitesimally small area in the exact centre of the field. One of Abbe's first attempts at the designing of microscope objectives purely by calculation appears to have resulted in a particularly bad specimen of this type. The search for the cause of the defect led him to the independent discovery of the famous "Sine-Condition," also announced almost simultaneously by Helmholtz, and previously discovered—without attracting the attention of opticians—by Clausius. In an approximate algebraical form it also figured as the second of the famous 5 conditions of Seidel. The realisation of its immense value, however, dates undoubtedly from the announcements by Abbe and Helmholtz in 1873. Since that time it has saved an incalculable amount of time and trouble to the designers of telescope and microscope objectives, as it indicates the presence or absence of coma in the central part of the field by a simple comparison of figures taken directly from the trigonometrical computations. I gave a simple and fairly exhaustive proof and discussion of this theorem in Monthly Notices for March, 1905, and to that paper those interested may refer.

If, and only if, the foregoing defects (spherical and chromatic aberration within the Rayleigh limit and coma) are properly corrected, then another defect of all ordinary lens systems will become obvious and objectionable, *viz.*, the secondary spectrum. This is due to the fact that, as compared with ordinary crown glasses, the heavy flint glasses which have to be used to compensate the primary chromatic aberration disperse the blue end of the spectrum too much and the red end too little. The result is that flint lenses of the proper power to secure achromatism for the brightest yellow and green region of the spectrum overcorrect the dispersion of the crown

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in the blue and violet end and undercorrect it in the orange and red end. As the crown lenses alone would bring violet to a shortest and red to a longest focus, the effect is that the achromatic combination brings both ends of the spectrum to a longer focus than its central part. Therefore there is a minimum distance of the focus for yellow-green, and at that focus the light from both ends of the spectrum is diffused, and causes a halo of a purple or claret tint. This halo is objectionable even in visual observations, because it falsifies the true colour of the observed objects, but the difference of focus to which it is due becomes a grave defect when the object is to be photographed, unless a strong screen is used which cuts off both ends of the spectrum, but more particularly the dark blue and violet light. Such a screen greatly increases the required time of exposure, and may be inadmissible in the case of stained or naturally strongly coloured objects, because these may be either opaque or too transparent to yellow-green light.

The attempts to produce varieties of *glass* free from this secondary spectrum have been unsuccessful as far as the microscope is concerned, for the existing crowns and flints with proportional dispersion have so little difference in dispersive power that an impracticable number of lenses would have to be used to secure the desired effect. We therefore still depend on the material whose value for this purpose was discovered by Abbe, the natural mineral fluorite, used instead of crown glass in combination with heavy crown glasses or very *light* flint glasses in place of ordinary *dense* flint glass. It was by the use of fluorite that Abbe produced the apochromatic objectives, and fluorite of good optical quality must be used to this day to secure the result. Apart from the difficulty of finding this material there is no obstacle to the designing by exact calculation of apochromatic objectives.

I now come to a defect of nearly all microscope objectives, and especially of highly corrected ones, which is well known to all practical microscopists, namely the pronounced curvature of the field, invariably in the sense of requiring a shortening of the distance from object to lens in order to obtain a sharp focus in the outer parts of the field of view. The general theory of the primary aberrations of oblique pencils shows that any lens system when freed from astigmatism will have the curvature of field defined by the Petzval theorem, and that in the presence of astigmatism the two focal lines which then represent the strongest concentration of the light always lie both on the same side of the Petzval curve and at distances from it which are in the approximate ratio of three to one. When the astigmatism is undercorrected the natural curvature of the field defined by the Petzval equation becomes aggravated whilst overcorrected astigmatism tends to flatten the field, and is deliberately introduced for this purpose in ordinary photographic objectives. The presence of considerable amounts of astigmatism, of course, renders really sharp marginal images impossible in either case, so that its absence or better still a modest amount of overcorrected astigmatism must be regarded as the ideal in microscope objectives. Unfortunately this desirable state cannot be reached in the existing types of objectives. The binary low power objectives up to the ordinary one inch and 2/3 inch come nearest to it, and are therefore justly liked

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by microscopists for all work for which they are sufficiently powerful. In the ordinary ternary objectives of the 1/6 inch type, with approximately plano-convex components, the curvature of the field is also of reasonably moderate amount. But it is a general experience that highly corrected objectives are very much worse as regards curvature of field. In the light of my most recent work on the general theory of lenses (Monthly Notices, November, 1919), this curious and objectionable peculiarity is easily explained, and becomes revealed as a *necessary* consequence of high spherical and chromatic correction if the usual number of components is adhered to. In the Lister and Amici types of ordinary objectives, which are fairly satisfactory as regards curvature of the field, the front lens is of such a form as to produce strong outward coma and there is in the back lens or lenses a corresponding amount of inward coma. The simple extensions of Seidel's theory given in the paper last referred to show that this is the state of affairs which tends to diminish undercorrected astigmatism or even to reverse it into the more desirable over-corrected form. High correction of the zonal spherical aberration, and to a still greater extent complete removal of the spherical variation of chromatic correction necessitate a more or less complete reversal of the coma effects in front and back components. In other words, with the usual types of objectives, reduction of curvature and apochromatic or semiapochromatic correction are completely antagonistic and incompatible: what benefits one correction is detrimental to the other. Fortunately the extended theory also indicates a way out of this dilemma. It appears fairly certain that by building the objective itself on the lines required by the apochromatic condition, but leaving it spherically undercorrected, perhaps also chromatically overcorrected to a moderate extent, and with a considerable amount of outward coma (this is the most important), and by correcting these residuals in a *widely separated* additional back lens, it will be possible to combine moderate curvature of field with apochromatic perfection and thus to remove the worst outstanding defect of the best objectives.

Condensers for the proper well-regulated *illumination* of microscopic objects are identical in optical design with objectives, the only difference being that the light passes through in the reverse direction and that a lower degree of correction is sufficient not only on theoretical but also on practical grounds, for nearly always condensers are used in conjunction with the " plane " mirror, which invariably is very far from optical perfection, and so introduces irregular aberrations of unknown magnitude and kind, and moreover the light from the condenser has to pass through the slide on which the object is placed. This slide is practically little better than window glass as far as optical quality and perfection of surfaces is concerned, and the great variation in thickness is another source of imperfection, especially with dry condensers of high N.A.

Moderate amounts of residual aberrations in condensers can always be effectively neutralised by using a sufficiently large source of light of uniform brightness or by magnifying the source by a sufficiently well-corrected " bull's-eye," if the source of light is naturally small.

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A great and very serious defect in the construction of nearly all condensers of the present day, with the exception of the modest "Abbe" Condenser of two simple uncorrected lenses, is that the Iris and the ring for dark ground-stops are placed too far from the back lens instead of being close to the anterior focal plane of the condenser. It is easily shown that such a remote Iris-opening or dark ground-stop produces decidedly oblique illumination of the extra-axial points of the object. With direct light this leads to an undesirable variation of the type of image and of resolving power in different parts of the field. With dark ground illumination the result is even more serious, for it is then necessary to use a far larger central stop to secure a dark background over the whole field than would suffice if the stop were placed close to the anterior focal plane of the condenser: such an unnecessarily large stop is highly objectionable, because it reduces the visibility of the coarser structures in the object.

The increasingly bad position of the iris in the condensers of higher power and shorter focal length supplies practically the whole explanation of the universal experience that high-power condensers will not work satisfactorily with low power objectives, especially for dark ground illumination.

The great thickness of the mechanical stage in English stands of the highest quality is the chief *reason* why the iris and "turn-out-ring" of high-power condensers have to be mounted so far below the back lens and a profound modification of the design of the stage with a view to making the part projecting over the condenser as thin as possible therefore appears to be the most desirable improvement of microscope stands from the optical designer's point of view.

In concluding these remarks on the optical design of microscope lenses I wish to point out that the whole subject is adequately dealt with in my lectures and classes at the Imperial College, and that students attending these for two or three years will be turned into competent designers, provided that they have a liking and natural aptitude for applied mathematics, are good at numerical calculations, and of an inventive type of mind.

As regards the *actual making of microscope objectives*, it must be borne in mind that the excellence of a computed lens system may be completely swamped by comparatively slight imperfections of workmanship, and that high accuracy in this respect is therefore of the utmost importance. In lenses of high N.A. computation shows that a departure from the prescribed radii and thicknesses by a fraction of a thousandth of an inch may lead to a notable loss of perfection, and the polished surfaces must also be truly spherical within less than half a wave-length of light. These limits can be easily observed if modern methods of gauging and measuring are adopted, and if all surfaces are polished to accurately made and conscientiously used test-plates. In the later years of my connection with the optical industry quite large batches of lenses used to be made directly from purely theoretical calculations of objectives of new types without any preliminary trials and without any experimental changes in the finished objectives, 95 or more per cent. of which would be found satisfactory in all respects just as they came

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from the mounters' lathes. The tools and methods employed in really *manufacturing* lenses on this system were shown by Messrs. W. Watson and Sons, Ltd., at the exhibition at King's College in January, 1917, and will be found described and illustrated in the record of that exhibition.

In old English practice the component lenses of microscope objectives and condensers used to be fixed in their cells by cement of the sealing-wax type. Many old lenses which are still found in perfect adjustment 50 or more years after being mounted demonstrate that the cement may hold the lenses in correct position almost indefinitely: but other experiences, especially with lenses used in tropical countries, suggest that shifting may occur, and it is therefore to be strongly urged that all microscope lenses should be held between metallic shoulders at both ends by being bezelled into their cells, care being naturally required to avoid pressure and distortion through too tight a fit.

A few words may usefully be addressed to the users of microscope objectives. All the higher powers are very sensitive (the more so the more perfect the spherical correction) to the thickness of the coverglass *plus any mounting medium* intervening between object and coverglass, and also to variations of tube-length, and the best result can only be obtained by adapting the tube-length (or the adjustment of the correction-collar if there is one) to the individual coverglass. It is grossly unfair to interchange one objective with another of similar power but different make on the tube-length suiting the objective treated as the standard and then to condemn the new objective (usually an English one!) because it gives an obviously inferior image. It is not even fair merely to find the best tube-length for the new objective, for if the change of tube-length is considerable and in the direction of lengthening, the total magnification will be much higher and the image correspondingly duller and more fuzzy. To make the comparison fair, each objective should be tried at its own best tube-length, and with such an eye-piece as to give practically the same total magnification.

Another point on which users of objectives err to their own detriment is an excess of faith in numerical aperture. I have heard microscopists boast of possessing an objective, say, of 1.43 N.A., whereas somebody else had one of only barely 1.40, and a careful test would show that whilst the 1.43 was an indifferent lens, the 1.40 was excellent. The fancied advantage of 2 per cent., then, is really a disadvantage of perhaps 25 per cent. or more.

One of the few disservices which Abbe did to microscopy was the pushing of the N.A. of dry lenses to .95 and to a lesser extent the increase of that of oil-lenses to 1.40. The extreme marginal zone of the apochromatic dry objectives of .95 N.A. is particularly badly corrected, so much so that the lenses will only bear a solid illuminating cone of about .65 N.A. even on the Abbe test-plate, and that with annular light bringing only the marginal zone into action correction-collar and tube-length combined do not allow of reaching a point of good spherical correction. There is no doubt that Abbe's own earlier dictum still holds, to the effect that beyond about .85 N.A. the higher aberrations become unmanageable unless the free working distance is reduced to a very few thousandths of an inch.

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A carefully computed objective of .85 N.A. will bear a full illuminating cone on suitable objects, and can thus realise its fullest resolving power. An objective of .95 with a condenser of .65 has the resolving power of the mean, or of .80 N.A., and is thus actually inferior except for freak resolutions with extremely oblique light. Oil objectives over 1.30 or at most 1.35 N.A. are also of very doubtful added value.

In closing this section I will once more quote without comment an anecdote of Fraunhofer, who received a complaint that a telescope supplied by him, although giving magnificent images, displayed certain fine scratches when examined with a magnifying glass! The reply sent by Fraunhofer is reported to have been:

"We have constructed the telescope to be looked through, not to be looked at."

A few sentences may perhaps be added as to the prospects for further improvements of microscopic performances. I have already stated in the first section that there is a bright ray of hope with regard to diminishing the curvature of field without loss of definition.

Advances in numerical aperture offer very little attraction. Abbe, in my opinion, carried the N.A. too far rather than not far enough, and I am not aware that any notable discovery has been achieved with the few monobromide-immersion objectives of N.A. 1.60 which he designed.

The use of shorter wave-length, *i.e.*, ultra-violet light, is a little more promising. There would be none but technical difficulties in the construction of lenses suitable for this work. But as only very few microscopists would be likely to go to the trouble of working in invisible light and of passing through a long apprenticeship in mastering the difficulties, apparatus of this description would necessarily be extremely costly, as the whole expense of designing and of constructing special tools would fall on a small number of outfits, or possibly on only a single one. And there would still be the grave drawback that the vast majority of objects would be opaque to extreme ultra-violet rays, and would only yield black-and-white outline pictures.

The so-called ultra microscope does not represent any advance in *resolving* power at all, but most decidedly the reverse. It is highly valuable for the detection of very minute particles and of their movements, which it achieves simply by intense darkground illumination, but the structure of the particles remains unrevealed, and only that would amount to an advance in resolving power. The seeing of these minute particles is, in fact, of precisely the same kind as the seeing of stars subtending less than .001 second of arc at night with the naked eye, the resolving power of which is of the order of 60 seconds.

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Professor Alfred W. Porter, D.Sc., F.R S., spoke on "The Resolving Power of Microscopes."

NOTES ON THE RESOLVING POWER OF MICROSCOPES.

By Alfred W. Porter, D.Sc., F.R.S.

The question of resolving power was first of all discussed in connection with telescopes; but the problem for microscopes is essentially identical with that for telescopes. The fact that telescopes of large aperture gave smaller star-images than those with small aperture was first demonstrated by W. Herschel (1805) and later by Foucault (1858). The explanation was given in terms of the wave theory of light by Fraunhofer (1823) and by Airy (1834). Owing to the wave structure of light, each image of a luminous point formed by a lens is found (both experimentally and by the wave theory as developed by Fresnel) to be a circular bright disc surrounded by dark and bright rings of intensity diminishing outwards. If there are two bright sources sufficiently close—two stars, for example—their individual discs may overlap; and for a certain degree of closeness the confusion is so considerable that it is impossible to detect the double nature of the source.

Some convention had to be adopted in specifying the limit at which separation between the discs can be appreciated. The convention actually adopted has been based on the fact that if the centre of the image of one star falls on the first dark ring of the other, then the brightest part of the combined image will be a figure-of-eight disc having a faint diminution of intensity at its middle, which reveals its composite character. Now the radius of the first dark ring (as calculated by Fraunhofer) is

$$\frac{1.22\ \lambda F}{B}$$

where B is the diameter of the object-glass and λ the wave-length of the light received. The angular separation of the stars when just resolved (according to the convention) is obtained (in radians) by dividing this by the focal length of the lens. The reciprocal of this is the angular resolving power. Practice has shown (Dawes; E. M. Nelson) that resolution is obtained when the sources are more than 25 per cent. closer than this. It was shown theoretically by A. W. Porter (R. Micr. J., 1908, Part I.) that the true limit (for which there would be no diminution in intensity at the middle of the double image) corresponds to a closeness of the stars for which the intensity curves would cross at their points of inflexion; this limit corresponds very nearly to that obtained from observation.

The question of resolving power is not, however, an exact branch of science. It is the "thing seen" with which we are concerned, and this depends upon who sees. The human element enters; and

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in consequence no exact statements can be made. All we can get is rough estimations by which the quality of optical instruments can be compared. The conventional limit probably supplies this desideratum as well as any other, and since it possesses greater convenience, it may continue to be adopted, except, perhaps, in special problems.

The problem of the microscope has been studied specifically by Helmholtz (1874), Abbe (1873), and by the late Lord Rayleigh. The name of the late Lord Rayleigh may be repeated, because he has dealt with the whole problem in all its ramifications in a way which no other investigator has done. In particular may be mentioned the following papers by him: "On the Diffraction of Object-glasses," Coll. Papers, Vol. I., 163 (1872), "Investigations in Optics," I., 415 (1879-1880), "Resolving Power of Telescopes," I., 488 (1880), "Wave Theory Light," III., 47-187 (1888), "The Theory of Optical Images, with special reference to the Microscope," IV., 235 (1896), Ditto (supplementary paper), V., 118 (1903).

The microscope problem possesses several peculiarities which are not met with in stellar observation. In the first place the object is never self-luminous like a star, and much depends upon the character of the light transmitted through the object when it is semi-transparent or reflected from it when it is opaque. Again, the object seldom consists of points (which would be imaged as diffraction discs and rings), but may be isolated or series lines or may be of any other shape; and in each case may be either bright or dark compared with the "background"; each case requires specific consideration. No one has worked these cases out in full except Lord Rayleigh, and reference must be made to his papers cited above for the full investigations. We can deal here only with some general considerations.

In the first place the essential difference in detail between a telescope and microscope arises from the object being near the objective. It becomes convenient to refer to the semi-*angle* that the objective subtends at the object and the distance, e (instead of the angle) between the two sources which are here separated.

Now for two independent points the distance e for which resolution will occur is for a rectangular opening

$$e = \frac{\lambda}{2\ n \sin a}$$

where n is the refractive index between the object and objective and λ is the wave-length of the light employed. On the other hand, Abbe, by considering a series of linear openings as object, found if the phase of the light passing through each opening is the same for all

$$e = \frac{\lambda}{n \sin a};$$

which is twice as great as before. The quantity n sin a he called the Numerical Aperture, and the reciprocal of e the resolving-power. These two examples bring out a necessary condition for securing fine resolution. The value of e is half as great as when the lights from different points of the object are independent, as when they are isophasal. Now this independence can be fairly secured by focussing a source of light by means of a condenser upon the

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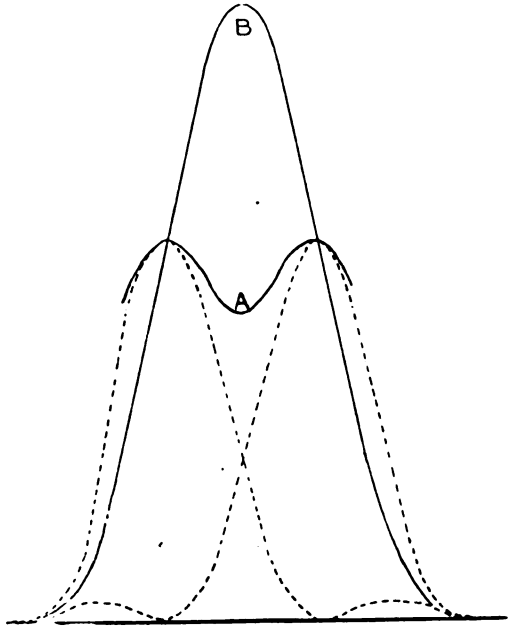
object. The condenser itself is an optical instrument to which the principles of resolution apply. The greater the Numerical Aperture (N.A.) of the condenser, the more nearly will each point of the object be seen by light from a distinct point of the source; but perfect independence is never secured. On the other hand, if no condenser is used, or if it be not focussed for the object, each point of the source will send light practically in one phase to a large patch of the object. Other points will do the same. Thus the independence between the lights at different points of the object breaks down, and Abbe's result will be approximated to. That is, for a dry objective ($n = 1$), instead of being able to resolve lines separated by $\lambda/2$ if $\sin a = 1$, their distance apart will require to be at least λ. It is this halving of resolving power which is brought about by replacing proper by random illumination.



The difference between these two cases may to some appear obscure. It depends on the fact that the light which passes through neighbouring openings in the object spreads out by diffraction and the diffracted beams overlap in the field of view. If there is no definite phase relationship between these beams the case is analogous to that of illumination by two candles—the *intensities* of light can then be simply added together. When there is a phrase relationship this is not the case. At points where there is an opposition in phase the resultant amplitude may be zero. At intermediate points the phase difference may be zero or a whole number of periods. In this case the resultant *amplitude* is the sum of the separate amplitudes and the intensity is the square of the amplitude. For the sake of illustration two such superposed illuminations are shown in the figure. The dotted curve represents the components placed so that the maximum of one occurs at zero of the other. The

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curve A is the resultant when the separate illuminations are independent, while B is the resultant when they are taken to be in the same phase. From A it might be inferred that the object was double from the presence of the two maxima in the resultant curve; in B the two maxima have merged into one and the resolution has vanished.

Examining, then, the case of two bright lines as the standard, it is seen that for a dry objective they must not be closer than half a wave-length for resolution under the best conditions of illumination. For the middle of the visible spectrum this means e = .000025 cms. For an immersion objective with immersion medium of refractive index n this should be divided by n. For light of shorter wave-lengths, e is proportionately less. Since this value is calculated (for simplicity) from the assumption that the lens aperture is rectangular, instead of circular, it differs very little from the limit given by the modified definition given by me and quoted near the beginning of this paper.

Magnification.

When an image is resolved it does not follow that it will be *seen* to be resolved. The division marks on a scale may be perfectly separate lines (much more so, in fact, than most optical images); yet they will not be seen separate if placed too far from the eye. It was stated by Helmholtz that they must subtend an angle between one and two minutes of arc in order to be seen as separate lines. In my own case and in those of about ten others recently tested the separation begins at about two minutes, *i.e.*, at shortest distance of clear vision, V, the lines must be separated about $\frac{V}{1800}$. This statement, of course, assumes that the eye can focus the lines in the position at which they are placed either without artificial aid or with the appropriate spectacles. It is also assumed that the illumination is good reading light. If the two lines in the image just resolved by a microscope objective subtend less angle than this, they will not be *seen* resolved. We can calculate, therefore, the limiting magnification necessary. An approximate calculation is sufficient.

With a total magnification of M_1M_2 the size of the image formed by the eye-piece is

$$M_1M_2.\frac{\lambda}{2}.$$

It is this that must be $\frac{V}{1800}$.

Hence limiting magnification is $\frac{V}{1800}.\frac{2}{\lambda}$

$$= \frac{25 \text{ cms}}{900 \times 5.0 \times 10^{-5} \text{cms}}$$

$$= \frac{10^4}{18} = 555 \text{ nearly.}$$

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This is the least total magnification necessary to reveal the structure in the case of this very successful resolution with a dry objective (N.A. = 1); and it is important to observe that it will only just reveal it. Now to see scale divisions well we do not place the scale so that they are only just separable. Even double the angular limit is advisable—and in some cases more. We may safely then take more like 1,000 magnifications for N.A. = 1, and up to 1,500 for N.A. = 1.5. This is precisely one of those data that cannot be definitely stated. We may, in fact, use 10 times the above minimum magnification in certain cases with advantage. But attention must be paid to one consideration in regard to which the graduated scale analogy is misleading. We bring a scale nearer not only to see the graduations easily, but to estimate small fractions of a division correctly. This presupposes that the marks are very fine—much finer than the interval between them. Now, in the image of an object whose structure is comparable with $e = \lambda/2$ there may be detail, but this detail is quite unlike the object. The artificial detail may be made clearer by extra magnification; but if the purpose of the observer is to find what the object is like, and not that of an investigator of the *errors* of optical images, the revelation of this artificial detail is useless and misleading. The only justification for excessive enlargement is when the image is thrown on a screen for inspection by a class, or similarly when a photographic print is made for the same purpose. In these cases it is intended to be observed from a distance; and the useful magnification is then such as will enable the true detail to be seen while the finer false detail will be blurred and inconspicuous. We must, therefore, distinguish between useful and useless magnification. It ought to be observed that it does not matter so far as this question is concerned whether the magnification is chiefly or *entirely* due to the objective. The eye-piece may be dispensed with, as is sometimes done in photomicrography; the calculation will not need any change.

This question should also be looked at from another standpoint. The eye-piece forms an image of the back lens of the objective outside itself; this is the "bright spot," or Ramsden circle. The rays that go through the bright spot are all those which penetrate the objective and are not stopped. The diameter of this spot is approximately $\frac{f}{T} \times$ diam. of back lens of objective, where T is the tube length and f the focal length of the eye-piece. Now in telescopes this can be larger than that of the normal eye-pupil with low powers, and in such a case only a part of the diameter of the object-glass is used. This can only happen with very low powers in microscopy. But with high powers (f small) the bright spot is very small, so that only a part of the pupil is effective. Now Helmholtz concluded that the normal eye-pupil will not bear much reduction without the image seen deteriorating, owing to imperfections in the eye. This point is not easy to demonstrate, because reduction in the aperture of the eye at first improves definition, since the eye is by no means free from aberrations. In my own case a fine line begins to be impaired when the pupil is limited to 2 mm. diameter by an artificial diaphragm. The decrease in sharpness

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proceeds only slowly at first, as the diaphragm is further reduced, and it is not until about one millimetre diameter that very considerable deterioration is noticed. The eye is itself an optical instrument. The radius on the retina of the first dark ring of a point source is about 0.01 mm. when the diameter of the effective pupil is 1 mm. This is about eight times the diameter of a retinal cone. But the total magnification

$$M = M_1 M_2 = \frac{T}{F} \cdot \frac{V}{f} \text{ nearly}$$

$$= \frac{V}{F} \cdot \frac{\text{diam. back lens of obj.}}{\text{diam. bright spot}} ;$$

or taking V = 25 cms. and 2 mm. as the diameter of the bright spot, the magnification becomes

$$M = 125 \frac{\text{diam. back lens objective}}{F} .$$

For the case F = 0.2 cms., back lens = 0.6 cms. diam.

M = 375 diameters.

If we suppose a reduction of the bright spot to 0.1 cm. diam. to be permissible M = 750 diameters.

These results are of the same order as before.

In the case of photomicrography, as we have seen, the permissible magnification is the same whether an eye-piece is used or not. There is the added advantage that the photographic image can be examined *with the eye at best aperture*. On the other hand, there is deterioration in the image due to the grain in the plate, by an amount varying much for different plates. Where the finest representation is required, it should not be forgotten that the old " wet " process could be resorted to; or, failing that, process plates are the next best.

The attainment of as close an approach as possible to perfect images is limited by the extent of the elimination of all the aberrations calculated by methods of geometrical optics. Professor A. E. Conrady emphasises the fact that extension of numerical aperture has surpassed the value warranted by the existing design and construction of lenses. The same may be said concerning condensers even more emphatically. Pioneer investigations on waves of non-spherical form were made by Lord Rayleigh and others. The variation of the intensity in the focal plane of a planoconvex lens has been worked out by L. Silberstein (Phil. Mag., Jan., 1918), who at the same time exhibits the general method by which all such problems can be attacked; and the same kind of question has been worked out by graphical integration by Professor A. E. Conrady (Monthly Not., R. Astr. Soc., June, 1919). Not only are the aberrations of the " lenses " important. The performance of a condenser is modified by the presence of a slide of very imperfect optical quality. So far as its inequalities in thickness are concerned, the errors arising are much reduced by the immersion medium when used with the condenser; a similar remark holds in regard to the objective and cover glass.

With biological specimens the objective " focusses " only a thin layer. If this is near the top of the specimen, the light from the condenser is scattered by the layers beneath; if it is near the bottom

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then the same applies to the emergent light. In either case there must be diminution of resolution. In the case of metallurgical specimens these defects are absent. The light is reflected from almost a mathematical surface. It may easily be, therefore, that for such specimens fullest advantage may be taken of permissible magnifying power, especially where the detail is of a simple character. This is seen, for example, in Figure 23 of the contribution by Sir R. Hadfield and Mr. Elliot, where the line markings of Pearlite are very clearly portrayed. On the other hand, in Figures 24 and 25, where there is evidently much fine detail below the resolution limit, it is not clear that the high magnification used is any advantage. Even if this fine detail appeared sharp, it would have no significance.

In the metallurgical case it must be borne in mind that if the mirror or prism in the vertical illuminator is opaque, it blocks out part of the aperture. The resolution of lines (such as those of pearlite) will be different, according to the azimuth in which they lie. Taking the aperture as semi-circular, the character of the image of a point is a central *oval* (instead of circle), the minor axis of the oval being parallel to the bounding diameter of the opening, and about half the length of the major axis (Struve, Mém. de l'Acad. des Sc. de St. Petersburg (7), XXX., No. 8 (1882); Bruns, Astr. Nachr., CIV., 1 (1883); Straubel, Inaug. Disért., Jena (1888); Scheiner and Hirayama, Abhand. Gesell., Berlin (1894); P. F. Everitt, R. Soc. Proc., A83, 302 (1910). Scheiner gives a photograph of the diffraction figure. Everitt gives also a diagram of lines of constant intensity).

Ultramicroscopy.

The considerations of this paper give no indication of the visibility of isolated particles, but only of the possibility of detecting their shape. If each gives sufficient light (either by self-luminosity, as in the case of stars, or by illumination by a powerful beam athwart the line of vision, as in ultramicroscopy), it will be seen. The amount of light it scatters is proportional to the *sixth* power of its radius when it is small compared with the wave-length. Its image is almost independent of its shape under the same condition. Under strong illumination larger particles ($<\lambda$) give complicated diffraction figures; but not much can be learned from attempts to interpret them. The visible disc is certainly much larger than the geometrical image of the particle. Similarly, a luminous line gives an image much wider than its geometric image. This case and that of an isolated dark line of finite width on a bright background have been worked out by Lord Rayleigh. In the latter case, when the background consists of light all in one phase, he concludes that the bar might well remain visible when the width of the bar is only one thirty-second part of the minimum distance between two lines for resolution. The slightly darkened image of the bar has then a width equal to about sixteen times that of its geometrical image and its apparent width is therefore quite illusory. In the case of a self-luminous background (*i.e.*, with phases completely independent), a bar of the same width has only half the visibility of the previous case, but it should be easily recognisable when its

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width is one-third of the minimum interval for resolution. He cites the following simple experiment: "In front of the naked eye was held a piece of copper foil perforated by a fine needle hole. Observed through this, the structure of some gauze just disappeared at a distance from the eye equal to 17 inches, the gauze containing 46 meshes to the inch. On the other hand, a single wire .034 inches in diameter remained fairly visible up to a distance of 20 feet or 240 inches. The ratio between the angles subtended by the periodic structure of the gauze and the diameter of the wire was thus

$$\frac{.022}{.034}\times\frac{240}{17}=9.1.''$$

He finds for the proportionate loss of illumination at the centre of the wire in this case

$$\frac{I-I_0}{I_0}=0.11$$

about what might have been expected.

The moral of these results is the recommendation of caution in interpreting even the width of the bars causing the streaking in microphotographs of pearlite, etc.

Besides the references in the text, the following may be given.

Airy, Tracts, 4th edit., p. 316 (reprinted as "Undulatory Theory of Optics"); Astr. Monthly Notices, XXXIII., 1872; Camb. Phil. Trans., 1834.

Foucault, Ann. de l'Observ. de Paris, t.v., 1858.

Verdet, Leçons d'Optique, t.1, p. 265.

Dawes, Mem. Astron. Soc., XXXV.

Ch. André, Etude de la Diffraction dans les Instruments d'Optique, Ann. de l'Ecole Norm., 1876.

U. Behn, u. W. Heuse, Zur demonstrations der Abbeschen Theorie des Mikroskops. Ber. d. deutsch Physik Ges. 4, 1906, Physik Z. Schr. 7, 750, 1906.

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Dr. R. Mullineux Walmsley, Chairman of the Technical Optics Committee of the British Science Guild, outlined the work of that Committee.

I shall not detain you more than a few minutes. I attend this afternoon, as you know, as representative of the British Science Guild, and I thank the President for his kind reference in his Address to that Guild. The Symposium, I take it, and I hope we all take it, will be an epoch marking symposium in the development of the microscope. If it be not that, I very much fear that all the labour which you, Sir, have put so fully into the organisation of this Symposium will not have answered its full object. That being so, however, I think it is only right to the Guild that I should give just the bare facts of its connection with the development of the microscope in order that they may be placed on record in the Minutes.

It was on 14th May, 1915, that the British Science Guild called a Conference of manufacturers and users of microscopes to ascertain what was necessary to secure to the British Empire, and particularly to the British Isles, the trade in these valuable instruments, a large part of which for so long a period had gone to other lands. Great Britain is historically and in many ways the home of the microscope. The Conference met. It was attended by representatives of the leading makers of microscopes in England and by representatives of Government Departments, including the War Office, the Admiralty, the Colonial Office, and the India Office, and by certain well-known private users of microscopes. The necessity for standardisation was the first point discussed, and was very generally recognised; I think there was not a single dissentient. Details were asked for, and a Committee was appointed, which met quite quickly, and elected for its Chairman Sir Ronald Ross, one of the most distinguished users of the microscope that we have. The Committee did not lose much time. The Conference was held in May, the Long Vacation intervened, but the Committee reported in October, 1915. It published, for further discussion, its draft specifications of three types of microscope, one for general use, and not very expensive; another type for advanced pathological work, and a third type for research work. It is not, perhaps, surprising that with a distinguished medical man at its head, the Committee had devoted special attention to pathological work.

These specifications were published, and criticisms came in. It was pointed out that they did not cover the whole ground, and therefore the Guild appointed another Committee to consider what other microscopes should be submitted to standardisation by definite official specifications. A Committee for Microscopes for Special Purposes was appointed, of which I have the honour to be the Chairman. This Committee was appointed in the late part of 1915, and it reported during 1916. The original Committee had confined its recommendations in regard to pathological work to expensive micro-

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scopes for advanced and research work. The new Committee, assisted, as was its predecessor, by manufacturers and distinguished users of the microscope—and for their assistance at both Committees the Guild is very grateful indeed—produced a specification for a student's petrological microscope, another one for general use in chemical laboratories, the cost of which was not to exceed £3 at pre-war prices; and, finally, a microscope for metallurgical work, in connection with which it had the assistance of distinguished metallurgists. These specifications were published during 1916 and circulated, but the trade determined that during the continuance of the war nothing could be done in the direction of standardisation until more quiet times came. The interval was not altogether lost, for these draft specifications were subject to criticism, and amended specifications, embodying considered modifications, have been drawn up, which we hope will be satisfactory to the trade and to users. The specifications will be published shortly.

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A group of papers on aspects of the manufacture of the microscope was then read by **Mr. Conrad Beck, Mr. F. Watson Baker** and **Mr. Powell Swift,** and discussion on these papers ensued.

A STANDARD MICROSCOPE.

By Conrad Beck.

The British Science Guild having prepared a specification for a standard microscope, we have been engaged for a year in working out the manufacturing processes necessary to produce on a productive scale a microscope that should fulfil the requirements of this specification. The instrument has also certain additional new features which will be appreciated by microscopists.

The stand, limb and body are of a very solid, well-finished type, with the horseshoe base, jointed pillar and Jackson-shaped limb. The base and stage are both coated with a thick surface of ebonite, the body has a larger tube than is customary; the drawtube is graduated, and gives a mechanical tube length of from 140 to 200 millimetres. The standard length of 160 mm. has been adopted for which all object glasses are corrected. The thickness of cover glass for which dry object glasses are corrected is .15 mm., or .006 inch. All object glasses except the very lower power are of such lengths as to be in focus when used on a nose-piece or an objective changer. The fine adjustment is of entirely new design, the two milled heads, one on each side of the limb, are on the same axis, but each milled head actuates a different lever, and thus there are two different speeds, one of which is double as fine as the other, both of which are always in operation. The convenience of this is apparent to those who use object glasses of different powers. A fine adjustment that is sufficiently fine for delicate examinations with 1/12 object glass is frequently troublesome in focussing 1/6 inch.

The action of the slow motion is by a screw with a point impinging on a lever. This method has been considered, and in our opinion correctly so, the only known method of obtaining an absolutely free movement without sag or backlash.

The base of the microscope is provided with three rubber pads which remove vibration, but which can be detached if a rigid contact with the table is preferred.

The instrument is supplied in its simplest form with a plain tubular substage with an iris diaphragm, but this substage can be removed by the microscopist himself and replaced by any of the three more elaborate forms of substage, thus converting the instrument into a complete bacteriological or research instrument.

With the same end in view, a detachable mechanical stage can be attached at any time by the worker himself. All parts are made to standard gauges.

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The base measures 6½ × 4 × 1 inch.

The distance of the stage from the table is 4¾ inches, which allows more room for substage apparatus than has been generally given.

The diameter of the mirrors is 2 inches, and they have a vertical adjustment of 1½ inches.

The stage is 4 inches across, and there is a free distance of 3 inches between the optic axis and the limb.

The instrument will carry the ordinary double and triple nose-pieces, but we have taken up a new object glass changer invented by Mr. Sloan, of Birkenhead, which we have found by prolonged use to possess many advantages over a revolving nose-piece, and by putting down tools we have been able to produce it at a very moderate price. The design is so simple and rigid that almost absolute accuracy of centering can be permanently maintained, and the errors of mounting of individual object glasses can be compensated. There are no slides, but the adjustment throughout is made by screwed abutment pins with clamping screws. Once these are adjusted and fixed they cannot shift, and the utmost error we have been able to detect in the alignment of the optic axis by the tightness or looseness with which the clamp by which the object glass and its fitting is secured to the microscope is about 1/6 part of the field of 1/6.

We have introduced a new micrometer eye-piece and a new system of measurement which appears to be in advance of previous methods. The object glasses are all engraved with an initial magnifying power, which is the magnifying power at the first image formed by the object glass with a tube length of 160 mm. We have designed a new vernier scale for measuring objects, with a special positive eye-piece which is entirely above the scale, and when this is placed in the microscope the scale is in the exact position occupied by the image which is formed by the object glass when the medium power eye-piece is used. The object under examination is measured in 1/10 of a millimetre on this scale, and the result divided by the figure engraved on the object glass gives the actual size of the object. If a stage micrometer be placed under the microscope, the initial magnifying power of the object glass may be checked, though this will only be necessary for very exact work. If a Sloan object changer is used, the drawtube must be set to 150 mm., or if a nose-piece is used it must be set to 145 mm. to compensate for the increase in tube length produced by these pieces of apparatus.

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At the conclusion of his paper **Mr. Conrad Beck** spoke on " Research in the Use of the Microscope."

RESEARCH IN THE USE OF THE MICROSCOPE.

By Conrad Beck.

In a series of lectures on the Theory of the Microscope which I delivered at the Society of Arts in the years 1907-8, I concluded with some remarks on the necessity for research on the use of the microscope. The methods upon which we now rely for the finest results obtained with high powers and for the best methods of illumination obtained with low and moderate powers are chiefly due to the work in the past of British amateur microscopists who have worked at the subject as a hobby and not as a profession. Now that the simpler problems have been solved, further improvements can only be looked for as the result of a combination of theory and practice which we can scarcely expect from any but trained research workers who can bring to the subject a combination of high optical knowledge and great skill in manipulation. Such work will, no doubt, require the co-operation of the manufacturer; but it is hopeless to expect that the manufacturer himself will have time to devote to the elucidation of the problems themselves. At the present time there are a large number of questions which will have to be solved before any very considerable progress is made in the science of microscopy.

In the lectures to which I refer I indicated, as an example of a possible direction for study, the ingenious suggestion of Mr. J. W. Gordon for reducing the size of the diffraction disc by the use of annular beams of light. This was only one point to illustrate the need of microscopical research. It is well understood that high power resolution depends on the aperture of the object glass, and yet in the new and extremely promising field of work opened up by dark ground illumination, we are deliberately reducing the aperture of our object glass to .9 or even .7 numerical aperture. There is no essential reason why an illuminator could not be devised by which much larger angles could be used in the object glass.

In the study of bacteria by dark ground illumination the diffraction images caused by the micro-organisms are extremely confusing, and there is room for research as to whether these images could not be profoundly modified by different methods of illumination, and to what extent the diffraction images indicate the structure of the organisms.

Another question, which, in my opinion, calls for serious research, is whether and to what extent a wide angle cone of light used in examining a histological specimen reveals or disguises structure, and to what extent the increase in brilliancy of illumination induced by opening up the aperture of the condenser increases or reduces the perfection of the image. I do not think there has been a satisfactory investigation on the examination of this class of

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object with different apertures in the condenser when a proper compensating apparatus for keeping the intensity of the light the same with all apertures in the condenser is employed. Neither has there been sufficient attention paid to the question of increasing or reducing the brilliancy of the illumination without varying the aperture of the condenser.

In metallurgical work, the method of throwing the light through the object glass on to the object is undoubtedly very effective, but every convex surface that the light meets in passing through the object glass must of necessity throw back a proportion of the light, thus fogging the final image. There is room for research as to another means of illuminating the opaque objects to eliminate this element of flare and ghost images.

This short paper is written to indicate by a few suggestions that we are more likely to obtain real advances in microscopy by setting up researches on the use of the instrument than by devoting the whole of our time to the discussion of the mechanical details of a slow motion or the most convenient diameter of a milled head. I cannot believe that we are likely at the present time to find a body of disinterested amateurs, with the required scientific training, to take up these difficult subjects. The subjects I have mentioned do not begin to cover the field of research that is required, and if this meeting could be made instrumental in the inauguration of this class of research, it will have accomplished an extremely valuable piece of work.

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PROGRESS OF MICROSCOPY FROM A MANUFACTURER'S POINT OF VIEW.

By F. Watson Baker.

The manufacturer, of necessity, is acquainted with the trend of microscopical development in every direction, for he is beset with suggestion and demand from workers throughout the world. The instruments he designs are largely moulded on his interpretation of such demands.

To a great extent there must be uniformity of design, but the expert, being usually a specialist, finds from experience that methods of work which he adopts as his own entail alterations of construction, and there is a tendency for such workers to attach importance to these details, and to recommend their incorporation in standard models.

It would be a matter of interest to see what the result would be if six independent leading workers were to prepare a specification of an ideal Microscope and Photomicrographic Camera.

English manufacturers have been in a position to meet the varied wishes of their patrons, because much of their work has been done by hand, and whereas with the machine-made microscope of the Continent and America the pattern has had to be taken as it stood, stipulations have invariably accompanied orders for all classes of English microscopes that certain features should be varied to suit the special views of those with whom the order rested.

Manufacturing in this manner has not tended to economic production, and, judging by the fact that it is possible to count all the manufacturers in Great Britain on the fingers of one hand at the present time, it will be fair to assume that such work is either unremunerative or involves difficulty or some disadvantage which discourages enterprise.

Past history reveals the fact that the development of the mechanical part of the microscope especially has been due to the British manufacturer, who has been largely directed and aided by notable progressive workers.

It is therefore not without interest to mention that thirty-eight years ago microscopes meeting fully to-day's needs, both in accuracy of working movements and stability of design, were made in this country.

When apochromatic objectives were first introduced, the only microscope stand on which they could be advantageously used was a British-made one. This alone had a fine adjustment worthy of its name and an efficient achromatic condenser.

Apochromatic substage condensers with means of centering them to the objective, the mechanical drawtube and the incorporated mechanical stage, together with the tripod form of foot, which alone gives stability in the instrument, were first made in this country.

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The British maker has always excelled in microscopes of high class, involving skilled hand-work. No instruments in the world to-day vie with the beautiful hand-made first-class microscope stands which have emanated from British workshops.

There is no question that this procedure has been highly approved by expert workers, who found in the best English microscopes the power to use their optical systems with an exactness and variety of adjustment which is not supplied so completely in instruments of other countries.

Students' microscopes, made by the same methods with constant variation, could not compete with standard models made by machinery.

It became evident, therefore, to those who were anxious to establish the English microscope on a sound basis, that a definite model for a definite purpose must be made, and a specification for each type not subject to variation drawn up to the satisfaction of those who directed the purchase and use of microscopes, thus justifying manufacturers in putting down plant for their production in large quantities under economical conditions.

A Committee was accordingly formed by the British Science Guild, consisting of representatives of the many branches of Science and Industry and Government Departments for which microscopes were required, and eventually definite specifications for students, research and other instruments were prepared, which have received universal approval.

This was a great step in a forward direction for the optical manufacturers. Works and manufacturing facilities had grown very substantially during the war, but the hand-workers of the past had been greatly reduced by dispersal and death, and it was no longer possible to make microscopes in sufficient quantity in the customary manner of bygone days. They were therefore able to apply much of their plant and machinery to the production of machine-made microscopes for students' use while reserving for the few hand-workers available the refined special work of first-class instruments.

The amateur, who has not had his requirements satisfied for several years, is pressing for supplies of the best patterns of English microscopes, but the quantity demand comes from teaching institutions, and particularly from medical workers. Of these latter there are a larger number than in pre-war days, and it is believed that the machine-made microscopes on the specifications referred to will be found satisfactory.

On the optical side, the production of microscope objectives and achromatic condensers has been fraught with difficulty. Very little, if any, of the pre-war optical glass remained, and the nearest substitutes had to be used instead, until such time as the British glassmakers were able to give all the varieties that were required for the purpose. Honour is due to them for the success they have achieved in making nearly all the types of glass that have been called for.

Even for a fresh melting of the same glass it is generally necessary, on account of slight differences, to make changes in curves or distances of components, but when several glasses by a fresh

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maker are dealt with, the sum of the differences in their constants, although the glasses are of the same *types*, necessitates the complete reconstruction of the objective. This is actually what is happening. It has only been during the last few months that the varieties of glass necessary have been delivered.

The computation of a high power objective usually occupies several weeks, and when this is done, proof plates and tools, which also require great care and a considerable amount of time in preparation, have to be made.

The full programme in this direction has not, therefore, been completed, but rapid progress is being made. The manufacturer is compelled to give priority to the production of objectives that are in most urgent demand, and those which by comparison are not so important will be made in full quantity as time progresses.

If the English microscope is to be firmly established, it requires now the whole-hearted support and recommendation of leaders in this country, and a generous patience while the preparation and supply of all that is needed is taking place.

The technical side of microscopy has, in this country, hitherto depended on two or three men whose names are well known. The means of education in practical optical science have been exceedingly limited hitherto, but it may be hoped that the instruction now being given in this subject will place at the disposal of the optical houses in the near future an increasing number of capable opticians. Such men must possess high technical and mathematical attainments, combined with practical knowledge which can only be obtained in the workshop.

There is one more point. The chief reason why the microscope is not manufactured by a larger number of firms in this country is, not merely on account of its technical difficulties, but because it is regarded as unremunerative. One large optical firm, at least, had microscopes in its post-war programme, but on studying the question, it was found to offer such small prospect of return for the effort and outlay that the project was abandoned, and financial men show no disposition to embark capital in a business of so highly technical a character. So it comes about that manufacturers are thrown very much on their own resources, and it is suggested that progress could be hastened and the whole business in microscope manufacture established in the fullest manner, so that it could stand four square to the competition of other countries, if capital were forthcoming on a generous scale for the purpose.

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A NEW RESEARCH MICROSCOPE.

By Powell Swift.

We have, in connection with Messrs. R. & J. Beck, been in consultation with Sir Herbert Jackson and Mr. J. E. Barnard concerning the requirements of a better research microscope for all classes of exacting work than has hitherto been made. This consultation has proceeded only so far as to deal with certain important aspects of the case. We think the advances that are likely to be made in the microscope will be due to constant discussions between the users and the manufacturers of the instruments, and in order that the discussions which have up to the present taken place should be materialised into something definite, we have prepared a model embodying the points that have been so far settled and which should form a stepping stone towards further progress.

Whereas a standard microscope can be produced which may satisfy the requirements of the ordinary worker for a reasonably long period, we do not think that the best type of instrument is likely to remain stationary as long as scientific progress takes place.

Therefore, in putting before you this stand, although we think it marks a distinct improvement due to the helpful suggestions that we have already received, we must take entire responsibility ourselves for the details, and merely express our thanks for the valuable assistance we have received from Sir Herbert Jackson and Mr. J. E. Barnard, without its being supposed that they can be held responsible for an instrument which we have made in order to exhibit at this meeting, without having had time to discuss the final details with them.

The first point which was considered was rigidity, and, while adopting the general principle of our "Wales" model, with its curved limb and radial means of inclination, the casting had been made with a metal tie of great strength to connect the portion carrying the body with that carrying the stage, so that when moving from the vertical to the horizontal position there should be no alteration in focus, due to the slight torsion which is otherwise produced in the curved limb.

The body is 2 inches in diameter, so that a photographic lens placed in its interior enables a large field to be obtained and not cut off by the margin of the tube. A rack and pinion drawtube and supplementary sliding drawtube are provided, so that the mechanical tube length can be varied from 140 to 250 mm. The fine adjustment, which is of the twin side milled head type, is fitted with Messrs. Beck's new double lever adjustment, providing in this manner two very delicate adjustments, one of which is five times as fine as the other.

The entire stage is carried on a very massive right angle cradle, and racks up and down, with all its apparatus for metallurgical work having a travel of 2¾ inches. This is more solidly constructed than has been the case with such instruments, so that there shall be perfect rigidity.

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The mechanical stage, which rotates concentrically, and is provided with centering screws for adjusting it to the optic axis, is a modification of that of our "Premier" model. The substage introduces an entirely new feature. It is provided with two cradles on the principle of the Sloan Objective Changer, introduced by Messrs. Beck, so that the whole of the substage apparatus, when mounted in interchangeable fittings with centering adjustments, can be instantly inserted in the substage, two pieces of apparatus being capable of insertion at one time. The body of the microscope is provided with a similar cradle, so that nose-pieces of a special character can instantly be interchanged if desired. For instance, the plain nose-piece may be replaced for petrological work with a nose-piece containing an analysing prism, Bertrand lens, quartz plate, etc., or with a nose-piece containing a high power vertical illuminator or other apparatus. The advantage of this system is applicable also to a great deal of physics research, as by introducing special apparatus into the substage or nose-piece, as occasion may require, a most perfect optical bench can be produced for general experimental work. There is a considerable class of delicate optical research which calls for an optical bench possessing the perfect adjustments of a microscope, and we believe that hitherto this requirement has not been met. By examination of the instrument it will be seen that almost any class of apparatus could be applied to the stand for making small and accurate measurements in physics, and although the chief object of this instrument is to provide the most perfect microscope that can be required, the other function for such an instrument has been borne in mind.

The base of the microscope is of the English tripod pattern, but has been provided with a new feature which is specially useful for photomicrography and optical bench work, which will also be appreciated by the ordinary observer. A hook shape casting is supplied which can be screwed down to the bench or camera, and an eccentric bar passing through the centre of the base will slide underneath this hook, when, by a slight motion of a lever at the side, the base of the microscope is locked firmly down in an exact position. Another lever between the uprights of the base clamps the joint by means of a right and left hand screw.

We have not alluded to the rack and pinion adjustments of the body, the stage, and the substage, which are of the usual spiral type, but might well call attention to the great width of the slides employed to give great stability to these adjustments.

It was decided in the consultations which took place towards the production of this microscope that while Messrs. Beck were employed on their standard instrument, we should undertake the manufacture of this special type, which would in all probability be sold by both the firms by which it is manufactured.

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General Discussion.

The Chairman invited discussion on the group of papers just presented, and he called on Mr. Barnard to make an announcement.

Mr. J. E. Barnard: The point that I wish to raise will only take a few moments. It is this, that Messrs. Swift, I understand, have quite recently manufactured a series of apochromatic objectives. There is no particular innovation in that, because they have made them for years, but I believe that they admit that in some small particulars they come short of the German standard. They are so conscious of the superiority of these new objectives, however, that they are anxious that a Committee should decide as to whether these new objectives are the equals, and we sincerely hope we may say the superiors, of those of German manufacture. For this purpose, therefore, they have suggested, and after consulting with Sir Robert Hadfield we have agreed, that a Committee should be asked to adjudicate upon them, and therefore Sir Robert Hadfield, as President of the Faraday Society, the Presidents for the time being of the Royal Microscopical Society, the Optical Society, and the Photomicrographic Society, and perhaps such an eminent authority in the application of objectives to metallography as Sir George Beilby and one or two others, are to be asked to go into the question of the actual value of these objectives. I feel quite sure that that is a proposition that will appeal to the meeting for the part it will play, apart from any other question, in perpetuating the work of this Symposium. Therefore, even if the results arrived at are not all we hope, this Committee and its conclusions will form a very valuable connecting link between this Symposium and any succeeding work. I therefore have pleasure in moving that this Committee be authorised to proceed with this question.

Mr. F. Watson Baker (Messrs. W. Watson and Sons): May I enquire whether apochromatic objectives of other English firms can also be included? We have made apochromatic objectives for some years, and are quite willing to submit them.

Mr. Barnard: I should say there is no question about that. The reason I brought this up was that Messrs. Swift are the only ones who submitted objectives under the conditions set out, but if any other firm is in the position to submit some, the Committee will be only too anxious to consider them.

Dr. R. Mullineux Walmsley: I am most interested in this question from the educational side. One of the main questions before the Symposium is the production of microscopes in large quantities, and I venture to suggest that, as Mr. Watson Baker says at the end of his paper, the colleges concerned must give him the necessary

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men for that work. I take that to be an absolute condition if we are to turn out instruments of high precision of this nature in quantity. The key of the situation lies in the inspection room of the factory, and unless the inspection room is adequately staffed with thoroughly trained men, the microscope manufacturers of this country cannot hope to rival what has been done—to which I refer with some diffidence in the presence of the President—in the engineering industry. Every engineer knows that the production of apparatus and machinery by the engineering industry—high-speed steam engines and things like that—has been due to efficient inspection by highly trained men in the inspection department. Parts are made in quantity, and are interchangeable, and the thing to aim at is to take the parts from store and have them fitted together without further adjustment by skilled workmen, and so to produce the finished article or machine. If the inspection department does its duty, we need not fear the competition of America or of France, both of which will be more serious than that of Germany in the near future; we need not fear it at all. The British microscope will then stand before the world and hold its own.

Lieut.-Colonel Gifford: In my experience I have worked out a good many apochromatic combinations, chiefly for telescopes, but I have never found any three glasses which gave a sufficiently long focus for microscopic objectives. That has led me to believe that the so-called apochromatic objectives for microscopes, excellent as they are, are not true apochromatics; I mean lenses which combine foci for three different portions of the spectrum. Whether that is so or not, I do not know, but I have met many people who know something of the subject who confirm me in this opinion.

Instructor-Commander M. A. Ainslie: This matter of the apochromatic objective has been occupying my attention for about 12 years, mainly from the point of view of what they would do in the resolution of very fine structure, and from the point of view of comparison between different types of objective. What put it into my mind to address the meeting was the fact that Mr. Swift just now was referring to his own objective. Mr. Swift a year or two ago was good enough to send me two 4 mm. objectives, one of which was entirely the equal of a perfect Zeiss 4 mm.; and I have some knowledge of Zeiss 4 mm. objectives, because I have used 18 of them on the same specimen, and I know that specimen by heart. One of the objectives sent me by Mr. Swift was fully equal to anything that Zeiss had done, but the other one was not. I presume that our English opticians are working, so to speak, to a standard. I know that they can turn out work which is in every way as good as anything that has ever been turned out in other countries; but while Continental opticians seem to have a habit of turning out what I might call objectives of 80 to 85 per cent. perfection, our English opticians seem sometimes to turn out something which is very fine—95 per cent.—but they often also turn out something which is about 60 per cent. perfection. In my experience in an amateur way, I have tested a very large number of immersion objectives, and of dry objectives with apertures from .4 to .95. I am

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bound to say that the English and other opticians I have had the pleasure of dealing with have put these lenses at my disposal without stint, but I feel that we want to strike a far higher average of excellence. We do not want 95 per cent. perfection in 10 per cent. of the cases, and the remainder under 60 per cent. We want to strike a 90 per cent. average and depend upon it. I want to mention that point because of apochromatic objectives which I have seen made by English manufacturers. I can single out a 4 mm. of Mr. Swift's, a 4 mm. .85 aperture of Mr. Watson Baker, and a 2 mm. of Mr. Watson Baker. I cannot tell you much about the latter, because I do not know what became of the lens, but it was a very perfect one indeed. I can fully echo any remarks that have been made as to the high quality of possible work of English opticians, but I also should like to mention that I wish they would always do it.

Dr. E. C. Bousfield: The few remarks that I shall make to-night have been prompted by what has already fallen, especially from Mr. Barnard, with regard to apochromatic lenses. I think perhaps my experience of them is longer than that of anyone here, since, in conjunction with my friend, the late Mr. Lees Curties, whose loss so many of us deplore, the first photographs made in this country with Zeiss apochromatic lenses were made in my own house, on a dining-room table, incidentally with the tunnel built up with books between the microscope and the camera, and the result was perfectly satisfactory. I think success in this matter depends comparatively little upon the brasswork, but a great deal upon the glasswork, and almost most of all upon the operator. The apochromatic lenses which were at first supplied were of the finest possible quality. I think I have seen nothing better than the first 2 mm. apochromatic lens which I had from Zeiss, but, unfortunately, as was the case with all these early lenses, the glass was very soon attacked by the atmosphere, and in substituting a glass which was more resistent, the qualities of the lens suffered very considerably, and when it was returned to me the field was very much less flat than it had been in the first instance. There is one maker who has not been referred to to-night, but who was absolutely, I believe, the pioneer of apochromatic lens work in this country—I mean the firm of Powell and Leeland. Certainly they turned out—and I say it without any disrespect to anyone else—the very finest work in the shape of glass-work that has ever been used in the world, and British glass-work has been of remarkable excellence. They supplied me, for trial, with an apochromatic lens of their own manufacture, which was calculated in England and made in England, and it was absolutely perfect, but it had the same fault that the Zeiss lenses had, in being made of unstable glass. None of the 2 mm. lenses that I have seen made of the more resistent glass are at all free from roundness of field. I notice that in one of the papers that is to be laid before us reference is made to this roundness of field, and in actual working, those of us who have tried it with, say, 1,000 diameters, will agree that it is a very serious trouble indeed, and I do not see any way of getting over it. Lower magnification and a longer camera does not do so. I suppose the reasons are mathematical ones, which are beyond me.

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I can only state the fact that if you get the same magnification with, say, a ½-inch lens and a long camera that you were getting with a ¼-inch lens and a short camera, you will hardly get more flatness of field in the one case than in the other.

There is just one other point, and that is that in all the photomicrographic apparatus which I have seen and possessed, there is one fault which seems to be inseparable from the instruments, and that is, with an extended camera, the connection between the operator and the focussing portion of the microscope, especially with lateral focussing milled-heads. These are extremely convenient, no doubt, for bench work in the laboratory, but for ordinary purposes of photomicrography it is extremely difficult to connect them satisfactorily with any form of extended focussing arrangement, and in any photomicrographic apparatus which may be put forward that point should certainly be kept in mind. The most efficient contrivance, I think, that I have ever seen—and the hint may be of use to some here, perhaps—was that of my friend, Dr. Neuhauss, of Berlin, who was well known as one of the very first photomicrographers in Germany. He simply carried a straight arm down from the axial focussing head of the fine adjustment, and attached a string to the lower end, with a weight on one side and a drum on the other, and so he managed to get his focussing fairly accurate. In conversation with Dr. Czapski once, when he came to see me, I pointed out to him that I found it impossible to get accurate focussing without tapping the bench, to make sure that the last adjustment was as delicate as possible, and he said, "Oh, that is quite the regular way for giving the final touch in delicate measurement"; so that I presume I had not gone very far wrong.

Lieut.-Colonel Gifford: I have in my possession two of these early Zeiss lenses. The late Mr. C. Lees Curties procured them for me at a very early period. One is marked No. 2, and is a 6 mm. of 0.95 N.A., and the other is a 3 mm. of 1.40 N.A., and is marked No. 34. Neither of them have suffered in the slightest, and I use them to-day as well as I did originally. On the other hand, I have Powell objectives. One of them is a 1/10 of 1.5 N.A.—a very large aperture indeed—and the other is 1/20 of the same N.A. The 1/10 became entirely obscured about two or three years ago. That, however, has been renovated by the present Mr. C. Lees Curties. The other one, the 1/20, has stood all through. At the same time, if you compare the two makers, I am afraid we must prefer the Zeiss. Both lenses which I possess of that make are simply perfect; I suppose they could not be quite perfect, but they are as perfect as they possibly can be. They stand any power you like to apply to them.

Dr. W. Rosenhain, F.R.S.: I want to draw attention to one particular point about the discussion which has impressed itself upon me in listening to it, and that is that there seem to be two totally distinct questions being discussed in a rather confused manner. The one is the question of establishing a commercial and industrial production of microscopes by mass production. This is, no doubt, a very excellent and valuable industrial step, with which, of course,

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every sympathy, and I wish it every success, and shall be glad to do anything to assist it. That is one thing, but the progress of the microscope as an instrument of research and an instrument of precision is quite another thing, and we must not forget the one in view of the other. It was particularly gratifying to find that whilst two of our manufacturing friends were good enough to come here this evening and to speak almost entirely of mass production, the third gave us some prospect of work which was directed towards achieving the best possible that could be achieved, and I hope that it will not only receive the acknowledgment which I am sure it will deserve at the hands of all users of the microscope, but that all manufacturers will feel, I think I may say, that it is their duty, to look after that side of the thing, just as much as to send out a cheap microscope by the thousand; I hope they will succeed in both.

Mr. A. C. Banfield (*Communicated*).

War considerations and other matters have prevented any active participation on my part in things microscopical for the last five years, yet, once having used a microscope, it is impossible entirely to lose one's interest in this important aid to scientific research.

One of the main objects of this Symposium is to suggest possible means of improvement to this instrument, and I will confine my remarks entirely to certain points which have occurred to me at various times.

(1) It is the custom at present, in all high grade microscopes, to supply them with two slides, which carry respectively the coarse and fine adjustments. This is an expensive form of construction, and as I am one of those persons of opinion that very little is mechanically impossible, it should be possible to eliminate one of these slides, making the single slide do duty for both adjustments. Also, as constructed at present, the fine adjustment slide is nearest to the limb, thus causing the delicate micrometer screw or lever to carry the weight of the parts necessary to operate the coarse movement in addition to that of the body tube—the only part the fine adjustment should move.

(2) It is hard to explain the preference which undoubtedly exists in this country for the tripod foot, rightly termed the "English" foot, for it exists in no other country. Many English manufacturers enthuse on "the beautiful hand work" to be found in their instruments, and I imagine that the tripod foot is especially designed to show this off. Now the universal trend in all modern manufacturing is to eliminate entirely all possible hand work; nothing adds more to the total cost of any article than operations which have to be carried out entirely by hand. My indictment of the tripod foot is that it is of a shape which is difficult to cast, and impossible to machine. It is, furthermore, very bulky, and seriously interferes with the efficient operation of the sub-stage when the microscope is in a vertical position. A greater rigidity is claimed for this foot; this certainly is correct if one wants to lean on the instrument, otherwise there is no advantage over the horse-shoe foot, resting on its three milled pads.

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(3) In most microscopes that I have used, the slides have been located in a position too near to the stage; the Continental makers are the worst sinners in this respect. The result of this practice is that when an object is focussed, the body tube has to be very considerably racked out, so that the slides only engage for about a third to half of their possible bearing. This does not add to the rigidity. The instrument should, of course, be designed in such a manner that with an objective in place on a changer, and focussed on an object, the male and female elements of the slide should be in complete engagement throughout their length.

(4) Even at the present state of mechanical advance, makers are still to be found preaching the virtues of the sprung slide. In the whole world of mechanics there is no more horrible device than this. It is supremely inaccurate and unreliable, and is merely adopted as an expedient to cover a state of residence in the dark ages of mechanics. Incidentally, I may remark, there seems a strange disinclination on the part of instrument makers to adopt modern manufacturing methods, the broaching machine, with the wonderful possibilities it holds out in the direction of dovetail and other slides, and eye-piece fittings appear to be quite unknown. Again, take such a simple job as a body tube. The common practice is to skim this in a bench lathe, then with the aid of a file and French cloth bring it to the lacquering stage—a tedious job, taking *quantum sufficit*, according to the workman. The whole job can be done on a modern grinder in a minute and a-half.

(5) Regarding the oblique illumination of metallographic specimens under high powers, it occurs to me that advantage may occur by reviving that old idea of fifty years ago in a modern form. If a glass rod, say a quarter of an inch in diameter and four inches long, is taken, and the ends squared and polished, it will serve to convey light from a source to an object with practically no loss. One end may almost touch an open arc, for instance, thus gathering rays at a high angle. These rays are carried along the rod by internal reflection (there is no need to silver the rod externally), emerging at the far end in a beautifully diffused bunch. This is no novelty to most of you, but I suggest that a variation of this idea may be of use in metallography. Take a worked slip, like a small Lummer plate, say 4 mm. wide and $\frac{1}{2}$ mm. thick. On one end balsam a hemi-cylindrical lens of 3 or 4 mm. radius. The other end can be introduced well under an immersion objective, not quite under but probably far enough. For this purpose, the slip would have to be silvered, except at the ends, otherwise the light would leave the slip at the first contact with the oil. At the other end, parallel rays are directed from some powerful source. I merely suggest this expedient for your consideration, as there appears to be a necessity for it at times.

(6) I have no practical acquaintance with metallography, but a specimen was sent to me a few days ago by a Sheffield firm. Now this specimen is distinctly spherical, and if specimens of this description are the rule and not the exception, I do not wonder that

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complaints "that the objective has not a flat field" are so common. The objective is computed for a mathematically flat object; if the specimen deviates from a true plane, then definition is bound to suffer. I merely refer to this point because it suggested to me an idea which it may profit some capable mathematician to investigate, which, briefly, is this:—

It is just as easy to prepare a metal specimen, worked to a definite radius, as it is to work it to a plane. Unfortunately, I am not a mathematician, but I suggest that by adopting some small concave radius for a metal specimen, say 10 mm., it may be possible greatly to improve the metallographic objective. The improvement may possibly take the form of a greatly simplified construction, or it may prove a means of increasing the N.A. of a lens. Personally, were I capable of it, I should compute it first of all unachromatised for use with the well-known Mercury line 5461, a powerful source of monochromatic light easily isolated. It could, if it showed promise, be further computed (all fluorite construction) for the powerful ultra-violet radiation at 1851. This would bring the N.A. for a 2 mm. lens to somewhere about 3.5.

(7) I have suggested the above (under 6) as a possible source of an improved objective for metallurgical purposes, but by working a specimen to a radius, it is possible to compensate an apochromatic or other objective which lacks flatness of field, by applying the well-known sphereometer formula.

Take a ruled stage micrometer, focus the centre of the field, and note reading on micrometer drum of the fine adjustment, after which take the reading of the alteration necessary to render the lines at the edge of the field sharp. Then if S is the semi-diameter of the circle in the object plane represented by the field of view, we can immediately say that if the object be given a curvature whose radius is

$$R = \frac{S^2}{2d}$$

the field of view will be in focus simultaneously at the centre and margin. d is, of course, the difference between the two readings of the fine adjustment drum.

A further group of papers dealing with various general aspects of microscope design and construction, presented by **M. Eugene Schneider, Professor Alexander Silverman, Dr. R. E. Slade and Mr. G. I. Higson,** and **Mr. R. J. E. Hanson** were taken as read.

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NOTES ON THE FUTURE OF THE MICROSCOPE.

By Eugene Schneider.

A. Mechanical Improvement.—It is very difficult to make precise suggestions as to mechanical improvement. The stands of the different constructors are approaching a type, which in a measure, tends to become classical. The initiative will in this development apparently have to be taken by the scientists and industrials. They will point out to the designers the defects of their instruments, and will indicate the modifications which technical progress requires. Yet we may specify one detail of improvement which might easily be realised. For a long time all designers have adopted the standard " universal screw " for the objectives. Nothing analogous has yet been done for the tubes in which slide the eye-pieces and condensers. This is frequently a matter of inconvenience to the microscopist, who possesses several instruments or who wishes to fit eye-pieces and condensers of different styles into his microscope and stand.

B. Optical Improvements. a. Eye-pieces.—As regards the optical parts, the microscopist, whatever his speciality, has all the necessary instruments at his disposal. At the outside, one might wish for eye-pieces of larger field for dissection or for the study of larger slides. That however, would necessitate a larger tube diameter. The field of the actual objectives is, moreover, of considerable curvature already, and one would gain little by trying to carry the observations to parts far away from the central portion.

b. Objectives.—Abbe has shown that the definition of the microscope is limited by diffraction effects, not on the edge of the objective, but on the object. He has established that the definition—which is frequently styled resolving power—is proportional to what he has termed " the numerical aperture," which he defined by the expression: numerical aperture = n sin u. There u is the semi-angular aperture, that is to say, half of the apex angle of the cone of rays passing through the object and admitted into the objective (Fig. 1), while n is the refractive index of the medium surrounding the front lens of the objective. More strictly expressed, n is the index of the least refractive substance which is found between the object and the second element of the front lens.

But n is a function of the wave-length. In order to increase the numerical aperture, and at the same time the theoretical range of definition, we may hence increase u, or increase n, or decrease λ

Dry Systems of Objectives.—The object itself is immersed in a medium of some refractive power, water, glycerin, Canada balsam, etc. But a cushion of air is always left between the cover-glass and the lens. As the refractive power of the air is taken as unit by opticians. the n in that cushion has the value 1, and hence the numerical aperature is equal sin u. In certain dry systems of apochromatic objectives, the numerical aperture attains the value 0.95.

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which corresponds to an angular aperature of 144° (compare Fig. 2). To go further in this respect appears to be impossible. On the one hand the rays would no longer issue from the point lens; on the other hand, the most oblique rays like 01. (Fig. 2) would strike the first dioptric plane at almost grazing incidence, and the losses by reflection would become very considerable.

Immersion Objectives.—Keeping the angular value of the aperture constant, the immersion increases the magnitude of n (Fig. 3). Cedar wood oil (n=1.52) is mostly made use of; it is interposed between the glass cover and the front lens. The numerical aperture may be raised to 1.40. In the great majority of cases nothing will be gained by exceeding this limit. Medical men, botanists, histologists and bacteriologists study their specimens when immersed in water, glycerin, salt solutions and, more rarely, Canada balsam. Only in this last-mentioned case they really utilise the total numerical aperture of their objective. For instance, when the object is placed in water, with a numerical aperture of 1.40, we have numerical

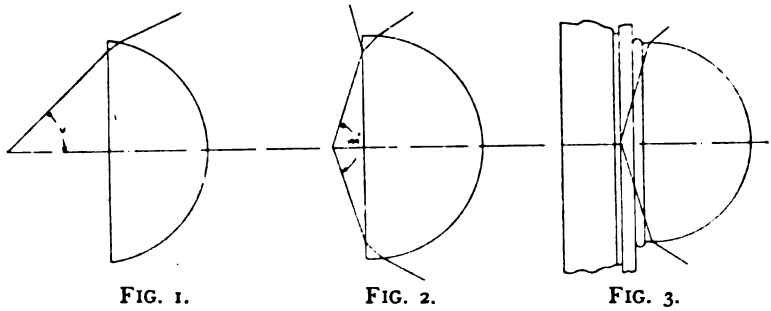

FIG. 1. FIG. 2. FIG. 3.

aperture utilised = 1.33/1.52 of total aperture = 1.22. The *conclusion* to be drawn is that, taking into consideration *only the theoretical definition* and the customary practice, one may say that the microscopic definition has already reached its limit. We have not referred to the variation of λ ; that point will be discussed when we pass to microphotography.

Special Cases. (*a*) *Diatoms.*—For diatoms and in general for very fine and refractory objects, we can make use of a medium and an immersion liquid of very high index. For the silica test of diatoms, *e.g.*, we can apply a solid medium of relatively high melting-point, as silica will stand high temperatures. In this way Zeiss has arrived at an objective of a numerical aperture of 1.60 in making use of a dense flint (for slip and cover) of monobromonaphthalene (immersion fluid), and a solution of arsenic sulphide in bromine (as medium). There again we seem to have reached the limit.

(*b*) *Metallography.*—In metallography the immersion liquid touches the object directly without interposition of any lamella. In this case there is no theoretical reason against the application of extreme numerical apertures; unfortunately the illumination problem becomes particularly difficult.

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Aberrations.—To a certain numerical aperture corresponds a certain limit of definition. But this limit is not always attained; in most cases aberrations distort the image, and the microscope proves inferior to what one might hope for.

Spherical Aberration.—This aberration can, in general, fairly well be corrected for a given radiation. The properties of the aplanatic points in the front lens facilitate the task of the constructor in a singular measure. When we consider rays of one colour only, there is little more to be achieved from this point of view with well-constructed objectives.

Sine Condition.—This condition—which says that, central aberration having been corrected for, the point images outside the axis are exempt from coma—is equally satisfied in all good instruments.

Curvature of Field.—As regards flatness, everything, or nearly everything, remains to be done. The field of better-class objectives is curved to a deplorable degree, so that it is impossible to make a useful observation on the borders of the field when adjustment is made for the central portion. The manipulation of the micrometer screw no doubt admits of rapid focussing and facilitates the successive exploration of different portions of the field. Yet there remains a loss of time and a certain difficulty in steadying the ensemble. The defect becomes more pronounced in photomicrographic work, though it can be mitigated by the aid of a projection lens, suitably corrected. But one must not indulge in illusions. As matters are and with the materials at the disposal of the optician, it is impossible to assert that we shall some day succeed in completely correcting for curvature of field.

Chromatism.—Chromatism is never eliminated, though it may be toned down. The so-called achromatic objectives, cut out of the customary glasses, always show more or less troublesome coloured fringes on the outlines of objects. Much has been written about the correction for *n* radiations by the aid of *n* glasses. When several conditions are written for achromatisation it can easily be recognised that the roots are real only for certain values of the co-efficients of partial dispersions of the glasses. In the very simple case of two glasses we may write: $\frac{\phi_1}{\nu_1} + \frac{\phi_2}{\nu_2} = 0$

or in another form $\frac{\phi_2}{\phi_1} = -\frac{\nu_2}{\nu_1}$

where ϕ_1 = the focal power of the convergent lens, ϕ_2 = the focal power of the divergent lens, ν_2 = the ratio of $(n_2 - 1)$ to the dispersion between the two radiations to be achromatised:

$$\nu_2 = \frac{n_2 - 1}{n_2'' - n_2'}$$ for the divergent lens,

and ν_1 = the same ratio $\frac{n_1 - 1}{n_1'' - n_1''}$ for the convergent one. If we possessed pairs of materials such that the ratio were independent of the chosen interval, we might with two glasses achromatise all the radiations. The pupils of Abbe have worked out this problem. The Jena glassworks have produced materials which satisfy the condition defined above *imperfectly*, but *better than the usual glasses.* The term *apochromatic* has

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been reserved for these instruments. Unfortunately the new flints, the telescope flint, boro-silicate flint, borate flint, etc., have small dispersive power. The lens curvatures have to be exaggerated, the zonal aberrations become disturbing, their correction is troublesome, the objectives are difficult to construct, and, in spite of their very real superiority over the ordinary achromatic objectives, the price of the apochromatc sometimes makes the buyer hesitate.

In our opinion, the progress of the microscope, as to *easy and compact correction of aberration, will depend much more upon the work of the glass-maker than upon the calculations of the optician.*

We can now form a clearer opinion concerning the interest which extreme magnifications of 5,000, 10,000 diameters and more can present. On Abbe's theory M. von Rohr has fixed the smallest distance that an objective of aperture 1.40 can resolve at 0.00015 mm. The eye can separate about 1 inch, say 0.1 at a distance of 33 mm. An enlargement of 700 diams. enables us to see all the details of an object. A more powerful eye-piece only enlarges the image without bringing out any further detail. The image which the observer examines may be less perfect than the normal view; on the other hand, the eye is fatigued by being strained to its maximum effort. For this reason, one has gone up to enlargements of 2,000 and 3,000 diameters. This latter magnification is excessive, however, and we have never seen it applied for any useful purpose in microscopy. In microphotography, on the other hand, it is sometimes serviceable to magnify 10,000 times and to use even higher powers—for instance, when the image is to be exhibited in the lecture theatre, or when one wishes to touch up a proof or to put references on it.

Photomicrography.—So far we have presumed working in ordinary light. As the photographic plate is sensitive to ultra-violet radiations, we can in photomicrography obtain higher definition by diminishing the λ. One difficulty creeps up at once, however: most of the optical materials are opaque to ultra-violet radiations. Rohr built up the whole optical system out of fused quartz; there was no correction for chromatism, and illumination was effected by one of the aluminium radiations. The index of quartz for D rays is n=1.54; for the ray Al_{γ}, the index rises to 1.69. The immersion liquid is glycerin; one is, in many cases, restricted by the opacity of the preparation itself. In these respects the limit seems to have already been attained, or nearly been attained.

Condensers.—As regards condensers, the constructors may be said to have preceded the microscopist. For delicate researches, non-corrected condensers are frequently used; yet they should be achromatic. The theory of Abbe assumes that the object is placed in the image of the luminous source. That is, with ordinary condensers, obviously possible only for one single radiation, and one point of the field. A bad illumination is so disastrous that, even at the present hour, many investigators are by no means convinced of the superiority of the apochromatic instrument. One cannot tell them often enough that this defect is solely due to the insufficiency of their condenser and to the poor choice of a luminous source. Achromatic, and even apochromatic condensers are in existence, and a *deplorable misjudgment* alone has prevented their general use.

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Metallography.—In metallography the objective serves as condenser. The illumination thus obtained may be perfect (especially with apochromatics), but the lenses are more or less marked, which somewhat impairs their definition. In any case, it is the illumination which will have to be studied for improvements. The problem appears to be singularly arduous, and a long time will no doubt elapse before the introduction of notable perfections can be hoped for.

Conclusion.—In a general way mechanical perfections of the microscope will naturally result from progress in micrographic technics. From the optical point of view we are restricted, at least in usual practice, by the impossibility of going beyond the numerical aperture of 1.40. Better correction of the aberrations and especially of the field curvature seem only to be possible by the creation of new optical materials. Finally, the use of ultra-violet rays admits of increasing the definition to a considerable degree; but the insufficient transparency of the media frequently imposes a limit.

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A NEW MICROSCOPE ILLUMINATOR.

By Alexander Silverman
(University of Pittsburgh, U.S.A.)

The device here described has already come into extensive use in the United States. The illuminator* and this paper are submitted for consideration by interested British societies.

The Lamp.—This consists of a quarter-inch glass tube containing a single tungsten filament. The tube is bent into a circle of one-inch inside diameter, and one and one-half inch outside diameter. It is made of colourless or blue (daylight) glass, and silvered, so that light is reflected downward from the circular source to the object being examined. The possibility of silvering the entire lamp and cutting a lateral line-slit in the mirror at the smallest diameter is under consideration to determine the possibility of producing through a plane of light a sort of ultra-microscope effect for the examination of bacteria.

The lamp is operated at 0.9 ampere and 13.5 volts for visual work, and 1.06 amperes and 18 volts for photographic work. Current from an ordinary lighting circuit is utilised, and controlled through a special rheostat (Fig. 1), which contains a push-button switch for the lower current and a spring-contact for the higher one.

The Holder.—An automatically adjustable support (Fig. 2), provided with three iris-like fingers, controlled by springs, is attached concentrically about the objective. The lamp is held to the underside of the support by two curved prongs and a perforated spring clip which slips over the exhaust protuberance of the lamp. The terminal wires from the lamp are attached to binding posts which are so constructed that they will also receive the brass pegs attached to the cord coming from the rheostat. These pegs may be inserted vertically or horizontally.

For general observation the lower portion of the lamp is in a plane with the flat face of the objective lens, but it may be raised or lowered to meet the needs of the operator.

Binocular Microscopes.—While the lamp-holder is clamped directly to the objective on monocular (Fig. 1), and single-objective binocular microscopes when 16 mm. or higher power objectives are employed, a stage support (Fig. 3) is provided for use with low power objectives and the Greenough binocular microscope. Lateral adjustment of the stage adapter centres the light and vertical

* U.S. Patents 1,311,185, 1,311,186 and 1,257,287, British Patent 125,187, Canadian Patent 185,283, Italian Patent 48/485, French Patent 489,304. Other foreign patents pending.

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adjustment enables the operator to keep the lamp at a constant distance from the object under examination.

The Shutter.—A shutter, which slips inside the lamp circle, may be placed under the lamp to cut off the light from one-half of the circle, so as to produce oblique illumination where this is desirable. Where depth without shadows is desired the shutter is unnecessary.

The Absorption Disc.—This is a dull black disc for covering highly polished surfaces, so that only the small portion under examination is exposed to the light.

Photomicrography.—For photomicrographic work the illuminator is attached as already described, and the camera employed without lenses, except those contained in the objective and ocular. For work done in this laboratory the camera shutter was left wide open. 16 and 32 mm. objectives were employed with a 10× ocular. As most microscopes are now equipped with vertical illuminators, the tube of such microscopes should be extended about 16 mm. when the vertical illuminator is removed and the new one attached. It is also desirable to use a Davis shutter in conjunction with the objective. Hammer ortho extra rapid plates were exposed for from 10 to 40 seconds, depending on the nature of the object photographed.

Low Power Work.—Excellent results have been obtained with low power objectives from 60 mm. to 16 mm. By using the stage adapter for 32 mm. and less powerful objectives, it is possible to place the lamp about one-quarter of an inch from the object and obtain beautiful effects. This is of advantage also with the double objective binocular microscope.

High Power Work.—The illuminator has proven satisfactory for oil-immersion work with a 1.8 mm. objective and 15× ocular (1,425 diameters). The markings on diatoms and structure of fine-grained alloys show clearly.

Heat of the Lamp.—To allay any fear concerning the heat radiated or conducted from the lamp, the writer begs to state that in his laboratory the lamp was attached to various objectives and run continuously at 100 per cent. over-voltage for more than half an hour without doing any harm to the objectives. Dr. E. M. Chamot, of Cornell University, conducted an independent series of experiments in which he drilled a hole in the side of the objective, inserting a small pyrometer tube between the lenses. He burned the lamp continuously over long periods, and pronounced it harmless.

Advantages.—The new illuminator, when used for the examination of opaque objects and others which may be viewed by reflected light, shows a greater wealth of detail than is obtainable by older methods.

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It is of special value for examining objects which possess light-absorbing surfaces, invisible under vertical light, which are beautiful under the new light. This is easily verified by viewing papers, textiles, leaf rusts, insect wings, potato mould, etc.

In metals and alloys it shows the depth of penetration of the etching medium, contrast, colour, and as Director Stratton, of the U.S. Bureau of Standards, has pointed out, it enables one to see the slag content of pits which appear black under vertical light.

The new illuminator may be used without removing the vertical illuminator. By switching the respective lights on in turn, valuable comparative studies may be made.

The illuminator, when attached to the objective or to a special arm of the stage adapter, may be lowered into hollow objects, such as the steel test dishes used in the enamel industry, or vessels used for the study of pond life, etc.

The illuminator is attached to the microscope, which may be moved without throwing the light out of adjustment. In photographing it vibrates with the microscope should the latter be jarred.

The new illuminator eliminates eye strain. The intensity of light which reaches the eye is lower than that produced by other methods. There is no polished disc to interfere with the vision, and only rays reflected by the object examined strike the retina.

Acknowledgments.—The writer desires to express his appreciation of the generous co-operation of microscopists who have experimented with the new device. He desires especially to thank your Mr. S. C. Akehurst for the pleasure of his company and valuable suggestions made during his visit to the States, and for his kindness in presenting this paper before the members of your society.

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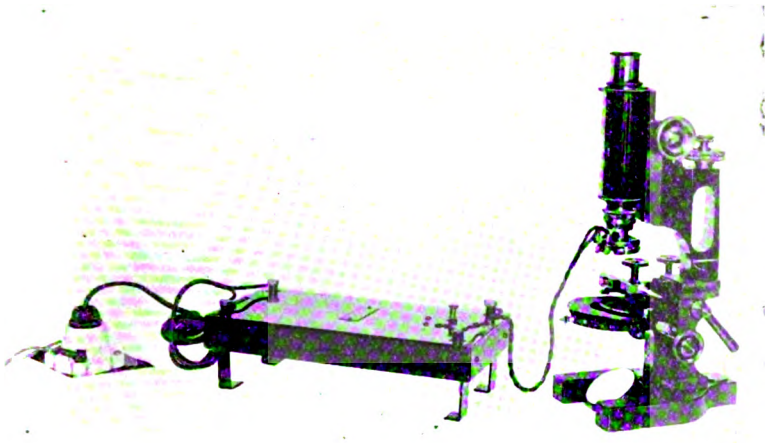

FIG 1.

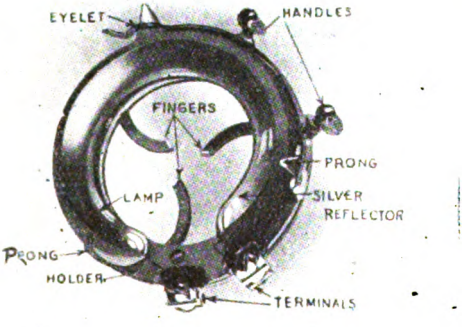

FIG. 2.

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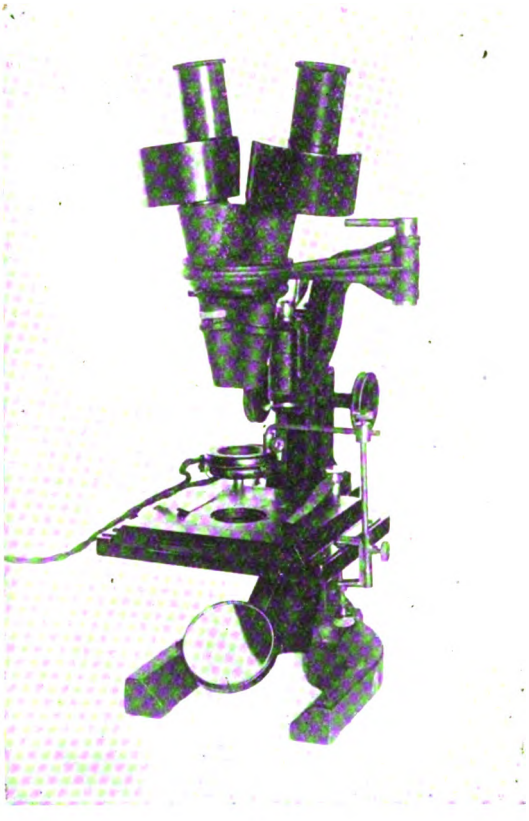

FIG. 3.

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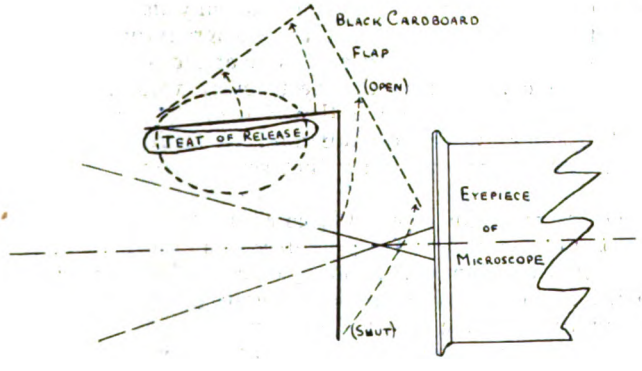
SOME PROBLEMS IN HIGH POWER PHOTOMICROGRAPHY.

By R. E. Slade, M.C., D.Sc., F.I.C., and G. I. Higson, M.Sc., A.I.C.

In an investigation of photographic emulsions we have found it necessary to take photomicrographs, using the greatest resolving power which we could obtain. In our attempts to overcome various difficulties inherent in different forms of apparatus, we have constructed an apparatus, which we believe contains some novel features.

The source of illumination is a 100 c.p. " Pointolite " lamp contained in a light tight box, a light tight connection being made between this box and the sub-stage condenser of the microscope, which is used in a horizontal position. Although this box is not ventilated we have not been troubled by heat from the lamp. No optical system or heat absorbing cell is interposed between the Pointolite lamp and the condenser, but an arrangement is fitted for introducing a colour screen in this position. The microscope is used with or without an eye-piece in



Action of Vibrationless Shutter.

a room which is totally dark, and the image is projected on to the plate, placed in a holder about one foot from the microscope, no camera being used. The whole apparatus is mounted on a solid block of ash. Focussing is done direct on to a piece of white card placed in the plate holder, a shutter is then brought down just in front of the eye-piece of the microscope, a plate put into the plate holder, and the exposure made.

This shutter, which is mounted quite separately from the base of the apparatus, consists of a roller blind shutter release, to the teat of which is attached a flap of black card (see Fig.), which is lifted clear of the path of the light rays by pressing the bulb of the release, exposure thus being made with complete absence of vibration.

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In order to surmount the difficulty of imperfect achromatisation of the lenses, a green filter is used and photographs are taken on process plates sensitive to this light. In all apochromatic lenses there is always a good deal of curvature of field, and we should like to suggest that for photomicrographic purposes it would be useful to have a lens without any colour correction, if the elimination of other forms of aberration and curvature of field would be thereby facilitated.

The illumination used is always what is usually termed critical, that is to say, the light source is in focus on the plate at the same time as the object being photographed, this being rendered possible by the uniformity of illumination over the whole of the light source. In this connection we should like to put forward a theory of the well-known phenomenon of the flooding of light over the image at critical illumination when the aperture of the condenser is fully open. We believe that the explanation of at any rate a part of this is that the image of the light source which lies in the plane of the object is not an infinitely thin plane, and there is so little depth of focus with a high power objective that we have the effect of the image of a bright surface lying just in front or just behind the object and out of focus on the plate, producing the so-called flooding effect. If we cut down the aperture of the condenser we eventually use only light which is almost parallel, and therefore obtain a shadow photograph which is absolutely free from flooding. If we cut down the aperture only a small amount we may do so sufficiently to make the effect of flooding negligible. In support of this we may mention that flooding is not obtained if the image of the light source is very much out of focus. In the " Pointolite " lamp the curvature of the light source will contribute to this effect.

In some of our earlier work we used an achromatic lens between the " Pointolite " lamp and the condenser, but it was the light source which was always brought to a focus on the screen, and not the image of a diaphragm over the lens, as is sometimes done. This lens was used to magnify the image of the light source so that a larger part of the object could be illuminated, but the same effect is now secured by bringing the lamp as close as possible to the condenser. In this way we can illuminate an area of the object, which is a little larger than the flat part of the microscopic field. This increases the ease of aligning the optical system, and moreover slightly increases the working distance of the condenser, which, however, is never much more than 1 mm.

The exposure with the orthochromatic process plates in use, with the green filter and a magnification up to 2,000 diameters, varies from 2 to 10 seconds. In this connection it is important to note that for all work requiring the greatest resolution process plates (i.e., plates with a hard working emulsion*) must be used. (Goldberg, P. J., 52, 302 (1912).)

Laboratory of the British Photographic Research Association,
Chemical Department,
University College,
Gower Street.

* In the December number of the *Photographic Journal* we have shown what type of emulsion is required to make a good process plate.

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FATIGUE FACTORS INCIDENTAL IN THE USE OF CERTAIN OPTICAL INSTRUMENTS.

By Surgeon-Commander R. J. E. Hanson, O.B.E., M.A. (Cantab.), R.N.V.R.

Fatigue—when it exceeds physiological limits—is one of the most potent drawbacks to industrial efficiency.

Moreover, it is usually of no sudden onset after commencing the use of optical instrument or projection apparatus, but is rather the result of summation of effect.

The causation of undue fatigue may be summarized under three headings:—

Section 1.—*Faulty environment.*

(A) Mal Hygiene of the home.

(B) Mal Hygiene of the workshop.

(In connection with "A," the influence of day and continuation school conditions to be reckoned with.

Section 2.—*Defects in the Eye.*

(A) Extrinsic, *e.g.*, Heterophoria.

(B) Intrinsic, *e.g.*, Ametropia, etc.

Section 3.—*Central and Psychological.*

(Or a combination of any, or all, the above.)

The illuminating engineer is at work to secure good lighting conditions, with beneficial results in many directions. Of great importance also are satisfactory conditions of ventilation, temperature and hygrometry.

In this short communiqué, I desire particularly to consider defects in, or misuse of, the muscular mechanism of eye movement, resulting in mal-orientation of the eyes, *i.e.*, Section 2 (A).

In the use of the bioscope one has opportunity to study the fatigue resulting from flicker; excessive contrast (defective retinal adaptation);* inadequate stimulation of the retinal periphery, and disproportion between dimensions and illumination of screen picture and the distance therefrom of the seat occupied by the observer.

The distance between audience and picture screen should not be less than 3 × D (D = diagonal measurement of the picture).

* The retinal periphery is best stimulated by means of clusters of frosted ruby (Fig. 1) coloured lamps suspended on brackets at intervals alongside the auditorium.

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If an observer sits in the " auditorium " *below* the level of the centre of the pictorial field of action, he is soon fatigued, and brow-ache and discomfort ensue, for observation requires him to *extend* his head slightly from the " primary position," to raise his eyelids and rotate his eyes upwards.

If now he reseats himself at a higher level (" dress circle " angle), these factors disappear, for now his head is in the " primary position," or slightly *flexed*, a position assumed by gravitation and requiring very little muscular effort for its maintenance.

It has been suggested that the lower seats in a bioscope theatre should be tilted backwards with head rests, so that the necessary

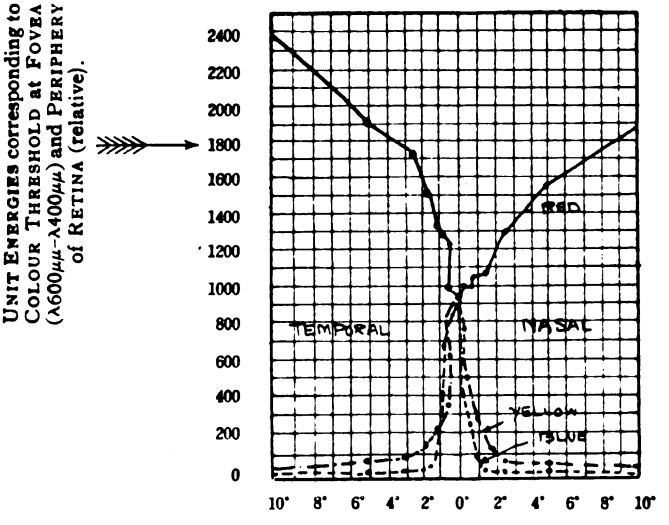

FIG. 1.

Diagram to indicate that the periphery of the retina is relatively less irritable to impact of radiant energy causing sensation of RED light, compared with the FOVEA (direct vision), observing that *the Adaptation phase (Dark or Light adapted) of the Retina does not affect the Red threshold.* The orange-yellow and blue (λ600-400) require the same number of energy units at their threshold of Perception, and are affected by the phase of adaptation of the Retina.

slightly extended position of the head may be attained without muscular effort and so avoid mal-orientation of the head and eyes. However, the promiscuous use of a head-rest in a place of public resort is not a feasible or pleasant proposition.

Fatigue factors, in connection with the observer's posture in using the *microscope*, are also present, and for him no facility is provided for resting his head and neck muscles, and insufficient attention is paid to the angle formed between the ocular and the vertical plane of the observer's head.

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In order to avoid mal-orientation and resulting fatigue, it is **necessary to provide the observer with a working bench of adequate height, correlated *height* and *position* of chair, suited to the physique** of each observer.

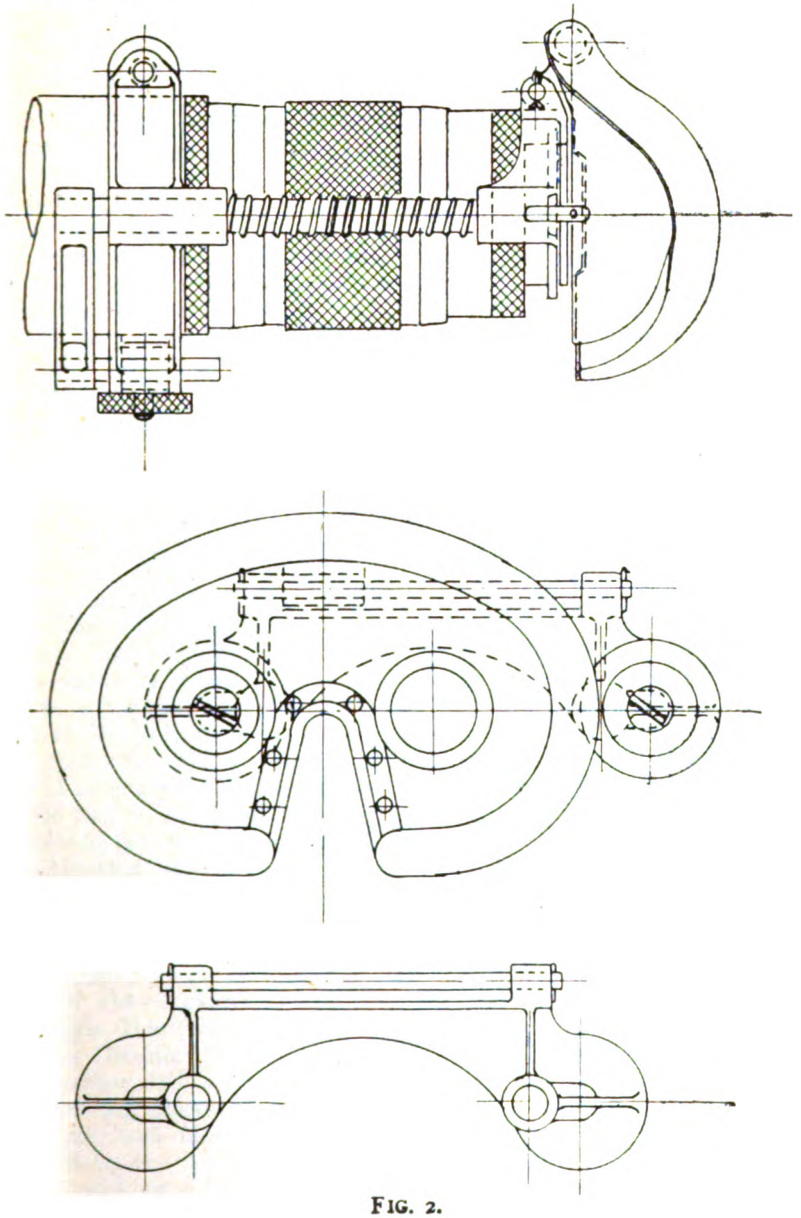

FIG. 2.

DYOPTIKON (PIVOTAL) HEAD-REST
(Universal Letters Patent).
Scale—One-Half.

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I have put in as an exhibit a working model of a headpiece attachable to any standard tube microscope without necessitating any structural alteration in existing patterns, although it is intended to arrange a bracket with attachment at or below the trunnion, in any new pattern microscope available. Diagram and models illustrating application of this dyoptikon head-rest (eye-piece) to telescopes, etc., are also shown. (Fig. 2.)

I am also showing, by permission of Professor A. D. Waller, F.R.S., his early and original negatives showing the electrical response of retina to impacts of radiant energy of short duration: also solution of so-called " Visual purple " which exists in colloidal solution bathing the receptor organ (retinal cones and rods), a photochemical substance which under the above circumstances of external stimuli presents a balanced reversible reaction, and has been shown to flow into the central fovea where no rods exist. Its " sensitivity " is in accordance with Planck's minimum quantum of energy, and has been shown by Victor Henri to be several thousand times more sensitive to light than the most sensitive photographic plate, on rapid exposure. Spectroscopically, " Visual purple " shows *no absorption bands.*

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A group of papers by **Dr. M. W. Travers, F.R.S., Dr. W. E. S. Turner, Mr. Robert Mond,** and **Mr. F. Twyman,** dealt with Optical Glass.

GLASS FOR OPTICAL PURPOSES.

By Morris W. Travers, D.Sc., F.R.S.

I have been associated with the glass industry since the outbreak of war, but the manufacture of optical glass in this country has been a matter of secrecy, and only officials have been admitted to the works, so that persons like myself can know only of what has been done indirectly and by rumour. British scientific literature contains one or two papers, indirectly connected with the subject, and the public and semi-scientific press contains only references to claims to discoveries of "German secrets" by British scientists—and denials that there were any secrets to discover. I hope that the claims are of a more substantial character than those put forward in connection with scientific glassware.

During the past autumn I made a tour of America, where I visited several of the new optical glass plants, to which I was freely admitted, and met many of the men who had been engaged in the development of the industry. During the early years of the war the manufacture of optical glass had been carried on in a rather desultory fashion, but in April, 1917, American industry was suddenly called upon to meet an enormous demand for optical glass. It might have been thought that America would have made use of the information gathered in this country, but an American scientist who took a leading part in developing the industry told me that this was not the case, for "we understood that your Government had a lot of information on the subject of optical glass, but we could get nothing out of them at all."

America was, however, in a very advantageous position from which to attack the problem. In the first place there were ample funds for research, administered by a thoroughly scientific body, the National Research Council, and not by a Government Department, scientific only in name. In the second place there already existed the organisation of the Geophysical Laboratory of the Carnegie Institution. Of the work of this institution the Report of the Director for the year 1918 speaks as follows:—"Suffice it to say that with a group of 20 scientifically trained men, all trained in handling silicate solutions at temperatures required for the making of glass, and familiar with the control of most of the important factors in the problem, it proved practicable to make rapid progress, and in June following, after two months of concentrated effort, the gross production of glass by a leading manufacturing firm had increased from 15,000 to 28,000 pounds per month, and in quality had improved to such an extent that rejections by Government inspectors became comparatively rare." The results are really expressed in the last sixteen words of the quotation.

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The rapid progress made in America was largely due to the fact that the scientists of the Geophysical Laboratory, and of the Bureau of Standards, were not content to sit on High Olympus in the suburbs of Washington, but did their work in the manufacturing plants, from which the results of their researches are issued. Thus science and industry co-operated in the closest possible manner, with results which speak for themselves; for not only were the practical results aimed at actually achieved, but a very large volume of scientific research was carried out, much of which has already been published in American scientific literature, while much more awaits publication.

We have certainly done good practical work in a limited field in this country, and nothing pleased me more than to hear the quality of some of our British scientific glass praised in America. The greater credit to those to whom the results are due, who have worked, as Englishmen often work best, in face of difficulties. Given the opportunity, the British scientist is equal to any in knowledge, and superior to most in grit; but the policy adopted by our Government Departments of attempting to monopolise science, and draw a dividing line between science in the university laboratory and science in the works, is fatal both to scientific and industrial progress.

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GLASS FOR OPTICAL PURPOSES.

By W. E. S. Turner, D.Sc., M.Sc.,

Of the Department of Glass Technology, Sheffield University.

It is with great reluctance that I find I must forgo the pleasure of being present at the Symposium on Wednesday next.

I am glad to know that some members of the Society of Glass Technology will be present and take part in the proceedings. The fine array of papers is a tribute to the great efforts Sir Robert Hadfield has made to direct the attention of scientific men to the importance of encouraging the production of all-British optical instruments.

Amongst the large number of papers, however, I do not find a single one dealing with the manufacture of optical glass. It is, in my opinion, unfortunate that there should not be as free and ready a discussion of this subject as had taken place in America in these past three years.

I should like to make some remarks of a very general character to indicate to makers and users of instruments the position in which optical glass makers frequently find themselves. There is, in my mind, not the slightest doubt that we can produce in this country all the types of glass requisite for microscopes and other optical instruments. The long experience of Messrs. Chance Bros., and the splendid achievements of the new Derby Crown Glass Co. undoubtedly demonstate this.

The amount of optical glass in any one instrument is, as a rule, quite small, whilst for the instruments of high precision, even the total amount of glass called for by manufacturers is very small. The glass maker, however, knows that in order to ensure homogeneity, freedom from striae, etc., from the glass, he must make a melt on a considerable scale. Further, some designers of optical instruments will call for a new glass of special properties, may be, for example, one which is successful in eliminating light rays between certain wavelengths. The production of such a glass calls for considerable research on the part of the glass manufacturer, and he usually cannot expect to sell but a very small quantity when produced, whilst the instrument maker is not prepared to cover the cost. Such a demand cannot always be met by the glass manufacturer; it is in no sense a commercial proposition. For some reason, connected probably with the early days of German competition, the manufacture even of the well-known varieties of optical glass has never been remunerative, although with the recent American products the prices, I believe, have had a more reasonable relation to the cost. One American manufacturer stated that he was prepared to continue the manufacture of optical glass if the loss was not greater than 10,000 dollars per annum, although he was hoping, eventually, the factory costs might be balanced by income.

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There is an obvious remedy for the unremunerative rates for optical glass, namely, that instrument makers should be prepared to pay prices sufficient to make the industry financially sound. There is also a means by which special glasses, required only in small quantities, may be made without asking glass manufacturers to go to unnecessary trouble and expense. It lies in the use of the joint resources of the laboratories of the British Optical Instrument Manufacturers' Research Association, under Sir Herbert Jackson, and of the Department of Glass Technology in the University of Sheffield.

The last-named Institution has been equipped in such a manner as to be admirably adapted for making special glasses in smaller quantities than the manufacturer can consider worth while, and meltings up to two cwt. in size can be undertaken. Where it is a matter of importance that a special glass shall be worked out, I urge most strongly that the joint resources of the two laboratories be employed.

In regard to crystals of calcium fluoride, I heartily concur with Sir Robert Hadfield's views that it would be strange if the mineral resources of the Empire could not furnish our requirements. Some time ago I received from a merchant, Mr. B. Moss, 21, King Street, Covent Garden, London, W.C., a beautiful specimen of crystalline calcium fluoride from a mine in the neighbourhood of Johannesburg. I am forwarding specimens of this to you. When I say that the specimen was sent with the object of obtaining a market amongst manufacturers of common glass articles only, it will be agreed that the source may be worth further exploitation for optical specimens.

The manufacture of optical glass in America, taken up only during the war, is still a long way behind ours in output and variety. Recently I was able to visit practically all of the war plants. The number of types of glass made so far is limited, and in the last few months all the plants except that of the Spencer Lens Co., at Hamburg, New York, and the new experimental plant at the Bureau of Standards, Washington, have closed down. For a long time, therefore, there should be in America an important market for optical glass made in this country.

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NOTE ON FLUORITE.

By Robert L. Mond.

Our Chairman, Sir Robert Hadfield, has asked me to ascertain whether crystals of fluorite suitable for optical purposes, of which there is a great shortage, are obtainable in the Dominion of Canada.

I at once got into communication with my friend, Mr. C. V. Corless, the General Manager of our nickel mines in Canada, who succeeded in ascertaining for me the following facts.

Crystallised fluorite is exceedingly scarce in Canadian deposits, and there only appears to be one property of any promise in Canada. Mr. Gavin M. Wallbridge, owner of the Wallbridge Mine, Madoc, Ontario, has sent me one crystal, which I herewith submit. In this mine there are two veins, which contain some beautiful, pure white crystals; he has supplied some of these crystals to Messrs. Bausch and Lomb, of New York. The crystal he has sent me he states to be from the second vein. This property is flooded at the present moment, and he cannot work it until next Spring. If material slightly off colour would be suitable, he would be in a position to supply straight away, but the clear white he could not supply before next Spring.

The vein is a closely packed one, tight from wall to wall, and in using dynamite to loosen the ore, all the crystals within a few feet of the shot hole are shattered. He is sometimes able, however, to locate a rough hole after mucking operations, and with great care and a lot of time he is able to save some beautiful specimens. He continues to state that the price which he obtained last year was so much less than the value stated by the Bulletin issued in Washington that he became disgusted, and did not bother to make any attempt to save the crystals.

He further states that he has not an expert there to place a value on the crystals, and, in consequence, must trust to the business honesty of the consignee. He has no doubt that a British firm would "play the game." He is much interested in the crystals end of the business, and would be very pleased to hear if the slightly off-coloured crystals would be of any use, and what would be the smallest size worth submitting.

I am also in receipt of a letter from Mr. Thos. Gibson, Deputy Minister of Mines, who has interviewed the brother of Mr. Wallbridge. He informs us that the deposit is very limited, and that the deposit not now being worked was much more promising. Mr. Gibson's impression is that we cannot count upon the Madoc Mine furnishing any commercial supply of the special type of fluorite, unless the demand is extremely small.

The material is undoubtedly fluorite, and I have submitted the sample to Messrs. Swift and Sons, who propose cutting a lens or prism from it to ascertain its optical properties.

Although the actual specimen is a large crystal, there are only relatively small portions of it which appear to me suitable for optical use. As this crystal was sent to me from Canada in a canvas bag, it may have suffered crushing in transit.

I regret I have not been more successful in obtaining information as regards the occurrence of this mineral.

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THE ANNEALING OF GLASS.

By F. Twyman.

Although owing to the small sizes of microscope lenses, and the fact that they are usually cut out of comparatively massive pieces of glass, want of annealing is very unlikely to cause the microscope maker any trouble, yet a few remarks relative to the principles underlying the annealing of optical glass may be of interest, if for no other reason than that the same principles underlie the efficient moulding of glass (or indeed of other materials), and there is no reason why an appreciable saving in the cost of manufacture of microscope objectives might not be effected by high quality moulding.

When the Research Laboratory of Adam Hilger, Limited, took up the question of annealing glass in 1915, we were unable to discover that any research work of a fundamental character had been done on the subject. We were unable to find even a clear presentation of the cause of faulty annealing. For various reasons we have not published a full account of the work, but the principles involved and some of the results as applied to glassware will be found sufficiently fully described in a paper read before the Society of Glass Technology in 1917. ("The Annealing of Glass," by F. Twyman. *Trans. Soc. Glass Technology*, 1917. I. 61, *et seq.*)

The phrase "badly annealed" when applied to glassware implies the presence of internal stress.

When glass is in a definitely molten condition there can be, of course, no permanent internal stress. Moreover, it can be shown, by keeping a suitable glass object under observation in a tube furnace, that even when the glass is cool enough to be practically solid under such stresses as are occasioned by its own weight, it may yet be mobile enough for severe internal stresses to disappear in a few minutes. On the other hand, at ordinary air temperatures glass is almost (though not quite) perfectly elastic.

But between this high temperature, where the glass is so mobile that internal stresses are evanescent in, at most, a few seconds, and the low temperatures, where the glass behaves as an elastic solid, is a region where internal stresses take, say, a minute, or an hour, or a few hours, to die out. It is this range of temperature which is important in annealing, and an accurate knowledge of the mechanical properties of the glass throughout this region is necessary if we are to attain any specified perfection of annealing in a minimum time, and without distortion of the articles. This region I call the annealing range.

If it were possible to cool any glass object from the high temperature down to ordinary air temperature in such a way that the temperature remained uniform throughout the mass, then no matter how fast the cooling the glass would be well annealed.

What actually happens is that differences of temperature exist while the glass is cooling. The stresses so caused are transient, so long as the glass is within the annealing range; but when eventually it becomes cold and the temperature uniform, there are present permanent stresses depending on the variations of temperature throughout the mass which existed while the glass was cooling.

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To anneal glass, then, it is necessary to keep it within the annealing range till the stresses have died out, and then to cool it with sufficient slowness. No kind of heat treatment which does not raise a badly annealed sample of glass to within this range will greatly affect its condition of internal stress, whether for good or ill, in any reasonable time.

The method developed in our laboratory for determining the annealing temperature will be found in the paper cited above. The steps in the argument may be briefly summarised.

The degree of annealing to be attained, and the time in which it is to be accomplished must be defined. For glassware we have laid down the condition that at the annealing temperature 95 per cent. of the original stress must disappear in three minutes. For optical glass appropriately modified stipulations are adopted.

The case of the disappearance of stress in a viscous body was considered by Maxwell,* who gave an exponential expression applicable to such cases connecting stress with time, thus

$$F = ESe^{-\frac{t}{T}}$$

where S is a distortion or strain of some kind produced in the body by displacement, F is the stress thus excited, E is the co-efficient of elasticity for that particular kind of strain, t the time, and T a time named by Maxwell the time of relaxation, which depends on the nature of the body.

The product ET he calls the co-efficient of viscosity, since in the case of steady progressive strain or distortion produced by constant stress the rate of strain multiplied by this product gives the stress.

It is obvious, then, that by defining the annealing temperature in the way we do, we have at the same time defined a viscosity. All we have to do, then, is to find the temperature at which the glass has the viscosity so defined, and we have the annealing temperature.

For details of apparatus and method the paper mentioned above must be referred to; but one point may be of interest.

It was found by us that in the neighbourhood of the annealing range most glasses examined double in mobility for every 8° C. rise of temperature, approximately. If then an attempt were made to anneal at 500° C. a glass whose annealing temperature (as defined above) is 580° C., the glass would require to be left one thousand times as long in the former case as in the latter.

The Research Laboratory,
Adam Hilger, Ltd.

* Phil. Mag. S 4. Vol. 35, Feb., 1868. p. 129.

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APPLICATIONS OF THE MICROSCOPE.

The following papers and communications dealt with recent developments in the applications of the microscope, particularly in industry.

This portion of the Symposium was introduced by the presentation of a paper on "The Great Work of Sorby," by **Sir Robert Hadfield, Bart., F.R.S.**

THE GREAT WORK OF SORBY.

By the President of the Faraday Society

(Sir Robert Hadfield, Bart., D.Sc., D.Met., F.R.S.).

Early Work; Researches on Metals; Researches on Rock Sections; Work on Meteorites; Application of Sorby's Work to Metallurgy.

In the First Sorby Lecture "On Some Structural Analogies between Igneous Rocks and Metals," read before the Sheffield Society of Engineers and Metallurgists in February, 1914, Professor W. G. Fearnsides, M.A., F.G.S., rightly said that the audience had met together to honour the father of Modern Petrography, that citizen of Sheffield, Henry Clifton Sorby. Professor Fearnsides has dealt with the subject in such an excellent manner and given so much valuable information in his lecture that I quote him very fully.

Early Work.—Sorby's earliest Research Work was in 1849 when he prepared the first rock slice ever made, and his first microscopical study of igneous rocks was presented in his historic Paper read before the Geological Society of London on December 2nd, 1857. His attempts were received almost with derision, some of the Members present saying that he was drawing largely on their credulity. Later he was thoroughly avenged by the Geologists of all Nations who assembled to celebrate the Centenary of the Geological Society of London when Sorby on the results which were formerly derided was acknowledged and acclaimed by them to be the founder of modern Petrography.

Researches on Metals.—Sorby began his work on Metals in 1863 and lectured about it in Sheffield before the Literary and Philosophical Society in February, 1864 ("On a New Method of Illustrating the Structure of Various Kinds of 'Blister Steel' by Nature Printing," Sheffield Lit. & Phil. Soc., 1864). Unfortunately there is no trace of this in the Proceedings. My own impression is that this Paper was

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one which was read before the National Science Section of that Society, but no copy was kept of it. When residing chiefly in Sheffield I was a Member of this Section, often meeting Dr. Sorby there. It is now no longer in existence.

Later on Sorby communicated his results at the Bath Meeting of the British Association ("On Microscopical Photographs of Various kinds of Iron and Steel," B.A. Report, 1864, Pt. II, page 189). In this Paper the Author briefly explained how sections of Iron and Steel might be prepared for the Microscope so as to exhibit their structure to a perfection that left little to be desired. He also exhibited a series of photographs taken by Mr. Charles Hoole illustrating the various stages in the manufacture of Iron and Steel and describing the structures which they presented. They showed various mixtures of Iron, of two or three well-defined compounds of Iron and Carbon, of Graphite, and of Slag; and these, being present in different proportions and arranged in various manners, gave rise to a large number of varieties of Iron and Steel differing by well-marked and very striking peculiarities of structure.

For 22 years the observations attracted little or no attention and when in 1877 Professor Martens, Berlin, and later M. Osmond and M. Le Chatelier, Paris, began to study metals with the Microscope they had to develop independently and anew the craft which Sorby had invented many years before. Sorby lectured on "The Microscopical Structure of Iron and Steel" at Firth College, Sheffield, in October, 1882, and stated that in view of the knowledge of fresh facts he had re-examined the whole of his specimens with improved Apparatus. In 1885 by the use of Lenses of high resolving power and large magnification he first discovered the true composite nature of the "Pearly Constituent" of steel as an aggregate of parallel plates, which discovery may be reckoned the crowning achievement of his microscopical research. Sorby announced this discovery to the Iron and Steel Institute in 1886, "On the Application of Very High Powers to the Study of Microscopical Structure of Steel," Journal of the Iron and Steel Institute, Vol. I, 1886, pages 140 to 144. Subsequently he presented to the same Institution his great Paper "The Microscopical Structure of Iron and Steel," giving a full account of his methods and the results he had obtained. (Journal I.S.I., Vol. I, 1887, pages 255 to 288). These Papers proved to be the signal for great activity in the field which he had so brilliantly started to explore, but it was really far back in the 'sixties that Sorby originated the Science of Metallography. His work at this period gave cause for an American writer in 1900 to say of him (in the "Metallographist" of April, 1900, Boston, U.S.A.): "Whatever has been accomplished since in microscopic metallography has been done by following in his footsteps. To Dr. Sorby and to him alone is due the pioneer's honour."

Researches on Rock Sections.—At the period (1849) when Sorby began his researches on rocks, the only available knowledge of the constitution of igneous rocks was that gained either by the field-worker with his hammer or by the indoor Geologist by the tedious processes of chemical analysis. Slices of rock

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ground to a thinness of about one-thousandth of an inch allowed light to pass, and with the Microscope it became possible to see their structure more clearly than the texture of the coarsest granite had hitherto appeared. Rock-slices, having been ground down flat, were admirably adapted to the application of polarized light, and to one who had already a working knowledge of optics, the vagaries of the vector variations of the optical properties of minerals proved to be no deterrent. Finding no treatise on this subject ready-made, Sorby designed, and, with his own hands constructed, a polariscope to work either with parallel or with convergent light, and the very instrument which he then made is still in use in the Sheffield University Physical Laboratory.

Researches on Meteorites.—Subsequent to his early Petrological Researches, Sorby turned his attention to the Microscopical Study of Meteorites.

In his Paper "On the Microscopical Structure of Meteorites" (Royal Society Proceedings, 1864, p. 333) he pointed out that he had applied to the Study of Meteorites the principles he had made use of in the investigation of terrestrial rocks described in his various Papers and specially in that on the Microscopical Structure of Crystals (Quarterly Jnl. Geol. Soc. 1858, Vol. XIV, p. 453). He there showed that the presence in Crystals of "fluid, glass, stone, or gas cavities" enabled the conditions under which the crystals were formed to be satisfactorily determined. There were also other methods of enquiry still requiring much investigation and a number of experiments to be made, but not wishing to postpone the publication of certain facts he gave a short account of them in this Paper.

This Paper was followed by another "On the conclusion to be drawn from the Physical Structure of some Meteorites" (B.A. Report, 1864, p. 70), in which Sorby pointed out that he had previously shown that the earliest condition of meteorites of which their microscopical structure furnishes evidence was that of igneous fusion. There were, however, some, like the Pallas Iron, consisting of a mixture of Iron and Olivine which apparently strongly opposed this view if judged from what occurred when melted artificially; for then the Iron being so much more dense would sink to the bottom and the Olivine rise to the top like slag in a furnace. The object of this Paper was however to show that this difference in density depended on the force of gravitation and that, on the surface of a small planetary body, or towards the interior of a larger planetary body, Iron and Olivine might remain mixed in a state of fusion long enough to allow of gradual crystallisation. Such meteorites should therefore be considered evidence of fusion where the force of gravitation was very small; and this conclusion might be valuable in deciding between rival theories of their origin.

Application of Sorby's Work to Metallurgy.—At the time these researches were carried out, although the Science of Metallurgy had advanced at a great rate, Chemical analysis remained the ultimate arbiter of the quality of any metal. The work, however, of Gore,

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Barrett and Tchernoff on the intimate relationship existing between recalescence and the hardening of steel, and also the work of Guthrie on eutectics led to the idea that both igneous rocks and alloyed metal are the products of the crystallisation of mixed solutions. Bunsen, and subsequently Vogt of Christiania, called attention to the laws which control the crystallisation of minerals in slag, and when Teall in 1888 pointed out the similarities of structure between graphic intergrowths and Guthrie's eutexia of Metals, the application of the solution hypothesis to rocks became apparent. In the domain of Metallurgy, the introduction of the Thermocouple by Professor le Chatelier led to the study of the Thermal Changes which accompany physical or chemical variations of constitution within the metal.

Sorby, in his Paper contributed to the Iron and Steel Institute in 1887 and published in Vol. I of the Journal for that year, stated:

"It is now twenty years since I commenced to carefully study the microscopic structure of Iron and Steel. The first object was the study of meteoric iron, but I soon found that the results were of even more value in connection with practical metallurgy."

Again, on page 276 of the same volume, he says:

"I regard that even a power of 400 linear fails to show whether the pearly constituent remains unaltered or broke up into very fine laminæ when very suddenly cooled. It either does not or the laminæ are too thin to be recognised. The changes in structure produced by hardening deserve far more study, but will I fear tax to the utmost the capabilities of the Microscope since the constituent grains of hardened steel are so extremely minute."

At this stage Sorby's work on Metals received recognition and exerted a powerful influence. It became evident that the mechanical properties of Iron and Steel depend upon the properties of their crystalline constituents, and at this period the nomenclature of metallography was developed. The subsequent work of Raoult, Van't Hoff, Gibbs, etc., led to a tendency to decry the nomenclature as unscientific. Nevertheless, it is still used and serves well for the ready specification of different qualities of steel.

Professor Judd, who was a friend of Sorby, has given some interesting reminiscences of the conditions under which Sorby worked. Apropos of Sorby's Laboratory, he remarked: "You speak of Sorby's laboratory. All his work, when I knew him, was done in a private room in his house; there everything was as simple as Wollaston's —a table with his Microscope, and a few bits of apparatus lying about."

In the same connection, Judd also remarked: "I went to Sheffield, as a Chemist to the Cyclops Works, straight from the Jermyn Street School of Mines in the Summer of 1864, and at once met Sorby. He not only taught me to make rock-sections, but showed me what he was doing with artificial irons—led to it by his studies of iron-meteorites. Mr. George Wilson, then manager of Cammells, a very enlightened man, gave me permission to supply Sorby with any irons that I analysed, for his work, so that I saw the beginning of his Metallurgical work—a very pleasant reminiscence. Down to the time that Ward

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and I left the Geological Survey, in 1871, Microscopic Petrography was always ridiculed by 'the powers that were.' They always said, 'You can't study mountains through Microscopes.'"

The following appreciation of Sorby's work is made by M. Ch. Frémont, the well-known French Engineer and Metallurgist:—

"It was Sorby's discovery of the method whereby the structure of a metal was laid bare to microscopic examination that gave him the right to the title. The method he used to prepare his rock sections failed him with metals, because the latter, even in very thin sections, are not transparent. Sorby, however, discovered that by suitably etching a perfectly polished surface of metal the structure was revealed to microscopic examination." The great merit of Sorby consisted in having applied to Metallurgy the Micrographic method he had discovered and introduced in the study of Mineralogy.

Our Meeting this evening is a living evidence of "Great is the Truth and it will Prevail." From the humblest of beginnings this method of research has grown into a giant. It will still further help to add to the sum total of human knowledge from which all may benefit. All honour to this Great Englishman for the magnificent work he accomplished.

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THE REQUIREMENTS OF THE PETROLOGICAL MICROSCOPE.

By Dr. J. W. Evans, F.R.S.

The Petrological microscope is constructed to serve two purposes. It is employed, in the first place, as an ordinary microscope, to observe the form and structure of the smaller features of rocks; and it is also used as an optical instrument for studying the action of minute crystals on light with a view to their identification. The latter function requires special features of greater or less complexity. The exact nature of these arrangements depends, however, to some extent on whether the material is examined in the form of a thin section of a rock, or in minute grains or fragments.

In all petrological microscopes provision is made for the examination of the object between crossed nicols, and for the rotation of these or of the stage or of both alternatively. The advantage of a rotating stage and stationary nicols is so great from the point of view of simplicity of construction, that it is always adopted in the cheaper instruments, and it is quite satisfactory in all cases where the work is confined to thin sections and methods involving certain special accessories or arrangements are not required to be employed.

On the other hand, for the examination of grains mounted in oil or other highly refracting medium, the use of a stationary stage and rotating nicols is practically a necessity, if high powers are to be employed, unless the Nachet device is adopted, by which the objective is attached to the stage and rotates with it. Rotating nicols are also necessary for the more complex optical methods, especially those that require an axis of rotation at right angles to the optical axis of the microscope, as when the optical characters of crystals are studied by means of the theodolite or " universal " stage. It deserves consideration whether, when rotating nicols are employed, a rigid connection between them should not be substituted for the gearing employed by Dick, even although the former is open to the objection that a rotation through a complete circle is not possible. This course has been occasionally followed.

Where crushed material or small grains are examined in oil or micro-chemical tests are applied, the microscope should be protected by a shallow glass bath with a plane floor, large enough to hold the glass slip.

There should be a " mechanical stage " providing for the movement of the object in two directions at right angles to each other and to the optic axis of the microscope, so that the position of the object may be varied while its orientation remains unaltered. These movements and the fine adjustment should be accurately graduated.

Arrangements should also be made by which a nicol may be placed in a position above the eye-piece. At the same time a slot should be provided at the focus of the eye-piece, so that accessories, such as quartz wedges, may be inserted in focus. The upper nicol or analyser, wherever placed, should be capable of rotation, either simul-

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taneously with the lower nicol or polariser or independently of it, and there should be special facilities for adjusting it at small angles of divergence from 3 to 6 degrees from the position of crossed nicols.* This is useful in determining the exact position of extinction.

Greater facilities should be given for the study of the interference figures in the " directions image " in polarised light. It is difficult to exaggerate the value of the purely qualitative results described by Beck, as well as the quantitative methods which involve careful measurements of the " isogyres " or dark bars.† For these purposes immersion objectives with an especially wide angle should be used with highly refracting liquids, and a corresponding wide-angled illumination should be provided. It is absolutely necessary that the student should be in a position to isolate the light from minute crystals surrounded by others of different composition or with different orientation. Among othr examples may be mentioned the zones and twin lamellae of plagioclase. By far the best means of effecting this is by inserting a diaphragm in the focus of the eye-piece and a Becke lens placed above it.‡ This should be a recognised accessory with all except the most elementary petrological microscopes. Provision should be made to enable the exact course of the isogyres to be measured. There is no space here to discuss the merits of the different devices which have been suggested, including one for which I am responsible.§

Some arrangements should also be available for the study of the object in linear convergent light, which is advantageous for various purposes. It can be obtained by employing an ordinary convergent system and inserting a narrow slit in a focus conjugate to infinity, with such orientation relatively to the object as may be required.‖

Provision should also be made for the use of monochromatic light when desired. The slit already referred to may be employed for the purpose in conjunction with a prism; or some form of monochromator, or a colour screen may be substituted, unless coloured flames be preferred.

I have not attempted to deal with all the numerous accessories which have been employed or suggested in petrological work, but have confined myself mainly to variations of construction necessitated by special methods.

Reference may be made to the report of the Microscope Committee of the British Science Guild giving a specification of a student's petrological microscope.¶

A serious difficulty is presented by the high cost of petrological microscopes constructed so as to allow of the application of advanced methods of research. This is inevitable so long as the number of instruments manufactured is too small to justify the employment of systematic standardisation with interchangeable parts.

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* F. E. Wright, Am. Journ. Sci., Vol. 26., pp. 349-368, 380-386 (1908).

† Min. Mag., Vol. XIV, pp. 230-234, 276-281 (1907); Min. Patr. Mitt., Vol. XXIV, pp. 1-34 (1905).

‡ Min. Mag., Vol. XVIII, pp. 45-51 (1916).

§ Mineralogical Magazine, Vol. XVIII, pp. 52-57 (1916).

‖ Min. Mag., Vol. XVIII, pp. 130-132 (1917).

¶ Journ. Brit. Sci. Guild; November, 1916, pp. 28-31.

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There are two directions in which we may look for an increase in the demand for instruments of this type. The first is the general adoption by chemists of optical methods of studying crystalline chemical products, and the second, the stimulation of the demand for British instruments in other countries. Every encouragement should be given to those engaged in original scientific work to design new or improved types of microscopes or accessories, and each new type should be fully described in the scientific and technical journals by the inventor, whether he is a member of the staff of a University or of that of an optical factory. If this policy is effectively pursued, other countries will turn to British makers for the supply of instruments of the latest and most novel patterns.

It was by such methods that the well-known German makers obtained the commanding position they held before the war, and it is only on these lines that our country can hope to take the place that it ought to have in the manufacture of specialised types of microscopes.

The working out of new ideas involves, however, considerable expense, far greater than is afterwards required to construct similar instruments when standardised and produced on a large scale, and it is absolutely necessary that pecuniary assistance should be, in the first place, forthcoming, if success is to be ultimately achieved.

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APPLICATION OF THE MICROSCOPE TO THE SELECTION AND CONTROL OF YEAST EMPLOYED FOR BREWING PURPOSES.

By A. Chaston Chapman.

The application of the microscope to the selection and control of yeast in the brewery may be said to date from the publication in 1876 of Pasteur's "Etudes sur la Biere." In this he made his famous pronouncements "That every unhealthy change in the quality of beers coincides with the development of micro-organisms foreign to brewer's yeast properly so-called," and that "the absence of change in wort and beer coincides with the absence of foreign micro-organisms."

By "foreign micro-organisms" in the above statements Pasteur referred solely to bacteria, and it was some years later (1879) that Hansen outlined his method of making pure cultures of yeast starting from a single cell. As a result of the application of this method, he showed that some of the yeast species which were frequently present, both in the pitching yeast of the brewery and in the air, were capable of producing "diseases" in beer quite as serious as those produced by bacteria. By a study of ascospore formation and other biological characters of the various species, it was found possible to make a distinction between the culture yeasts and the so-called "wild" yeasts sufficiently definite to enable one cell of the latter to be detected in the presence of at least 100 cells of culture yeast. By means of the microscope, therefore, it is possible to detect the contamination of the pitching yeast, not only with bacteria, but also with other undesirable yeast species, and to take the necessary steps to purify it.

Lantern slides representing culture yeasts and a number of the "wild" yeasts in illustration of the above statements were shown.

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THE MICROSCOPIC OUTFIT OF A TEXTILE RESEARCH LABORATORY.

By R. S. Willows, M.A., D.Sc.

In the interests of brevity I will confine my remarks closely to the requirements of a research worker in the textile industry. The materials to be examined are fabrics, yarns, fibres, starches, and

Objectives.

The objectives used will be from 2 in. down to an oil immersion, and for certain purposes an ultra-microscope of the cardioid or similar type, while for special work an immersion ultra-microscope may be a great advantage. The most useful lenses are the 16 mm., the 6 mm., and in a less degree the 4 mm. and an oil immersion. The first is most useful for examining single fibres, while the second will do most of the routine work on sections, especially if it will stand a high power eye-piece. Strange to say, at least one English maker of high-class lenses does not produce a 6 mm. lens. I have found certain English apochromats excellent in flatness of field and definition, but they have the disadvantage of a short working distance; it is fair to add that in the last respect they are no worse than Continental types. For most purposes I find some semi-apochromats in my possession are all that is required; the field is not very flat, but the definition in the centre is excellent, their working distance is large, they will stand an ×18 eye-piece, and they are comparatively inexpensive.

Stands.

I prefer the English type of stand to the Continental model, on account of the better distribution of weight and consequent greater stability, and also for the greater space for the substage. The tube must rack out to take a 2 in. objective, and in this connection it is a great advantage if the stage can also be racked. The latter movement is also very useful when it is required to use vertical illumination. A mechanical stage, centering substage, and high-class condenser are taken for granted, even on the simplest types of stand. Very frequently a considerable portion of the slide has to be examined; this should be possible without fouling the condenser.

As the material to be examined has frequently to be submitted to the action of acids and alkalis while it is on the stage, the latter should be made of a suitable material, and should be designed so as to eliminate as far as possible the chance of injury to the instrument. Apart from material used, the design of such a stage appears to have received little attention. It is in such examinations that a large working distance for the objective is so markedly advantageous.

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Polarisation Apparatus.

This is often extremely crude. Types which require the analyser to be screwed on behind the objective, or in which the polariser replaces the condenser, not only waste much time in making the necessary changes, but the illumination is cut down badly. The analyser should be built in the body tube, should be capable of being swung or slid out when not required, and the analyser should come below the condenser and should have the swing-out motion.

Ultra-microscope.

An efficient and easily handled form of ultra-microscope is urgently required, not only for general scientific research, but also in several branches of textile work, especially on the sizes and dyes.

Photomicrographic Apparatus.

It is on this side that English apparatus is most defective. Where it is not a frank imitation of foreign types, it shows no evidence of design as a whole, and in a number of small details is so defective that I sometimes doubt if its makers have ever used it to take photographs under the varied conditions that exist in a works research laboratory. For my own purposes I desire an equipment fulfilling the following conditions:—

(1) As it will be used where there is considerable vibration, the mechanical design should be such as to reduce the effects of this vibration to a minimum. That eliminates the type where camera and microscope are on separate stands.

(2) It should be easy to make a visual examination before the photograph is taken. This is most readily done by swinging the optical system and microscope out of line with the camera. It may be difficult when the light source is a large arc surrounded by a lantern, but is comparatively easy if a "Pointolite" set is used. I have found this source most efficient and handy. It consists, as is well known, of a tungsten arc in nitrogen; it burns for hours without the slightest attention, and as the spectrum of tungsten is exceptionally rich in the photographically active rays, it is more powerful than a simple candle-power measurement indicates. May I suggest to manufacturers that before it is fixed on the optical train they should discover in what direction it emits most light, and fix it accordingly? At present the direction used appears to depend on other considerations altogether.

(3) It should be possible to pass from transmitted to vertical illumination quickly and without having to make a number of delicate adjustments. Among the unsatisfactory methods at present put on the market I have come across the following:—(a) Change the microscope to a vertical position and use a vertical camera; (b) swing the optical train through a right angle round a vertical axis; (c) move the optical bench parallel to itself and insert a mirror inclined to the beam at 45°. The last is undoubtedly the method requiring the least complication of apparatus if properly designed;

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but some of the applications of it are very crude. A fourth method appears to be possible, *viz.*, to keep the optical train fixed, but to deflect the light three times at right angles by total reflexion prisms, and so throw it into the vertical illuminator. As the last prism would be a small one, it could well be carried by the moving part of the microscope; it would not then require adjustment as the microscope is focussed.

(4) It would be a great advantage where the action of solutions is to be followed and recorded, if a horizontal camera could be used when the slide carrying the object is horizontal; this would combine the advantages of a horizontal camera and a vertical position for the microscope tube. I have not seen any attempt at this in an English apparatus.

In conclusion, may I say that the textile industries in the past have been among the least scientific of the large trades, but the need for research is now fully recognised. In such research the microscope and physical apparatus generally must play an important part. As one who is keenly interested in the technical applications of science, I hope instrument makers will make themselves acquainted with the requirements of the industry and will endeavour not only to meet them, but, if possible, to anticipate them. As a small step in this direction I suggest that *The Journal of the Textile Institute* should find a place on the shelves of their works library.

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A series of papers dealt with the use of the microscope in metallurgy. The subject was introduced by **Dr. W. Rosenhain, F.R.S.**

In view of the lateness of the hour, there will not be time for me to read the paper which I have prepared; therefore I will only deal with one or two points which I think are more relevant to the aspects of the whole question which have already been discussed. I should like to say one or two words with regard to the question of increased magnification and increased resolving power for metallurgical work. There can be no question that we are dependent to a large extent for further progress in certain directions in metallography on obtaining higher resolution and higher magnification, but it has been clear to many of us for a long time, and to those to whom it has not been clear it will be so after having listened to these discussions, that magnification alone is quite useless, and that what we must look for is higher resolving power. Mr. Barnard has emphasised the theoretical possibilities of using a much shorter wave-length. No doubt in the future it may be possible to do that, and Mr. Barnard himself has been singularly successful in utilising the short wave-length of invisible light for photomicrographic work on transparent sections. About seven or eight years ago I was able to obtain at the National Physical Laboratory a complete outfit of Zeiss apparatus for this purpose, and I spent a large amount of time—over a year—in endeavouring to use it for metallographic purposes, but the result on the whole was extremely disappointing. I succeeded in getting a few photographs, but the time occupied and the labour involved were enormous, and when I did succeed it was only with moderate magnifications. The attempt to use high power monochromatic immersion lenses failed entirely, owing to the fact that I always got milky images. Fluorescence occurred whenever the ultra-violet light struck any object within the tube. When the beam of ultra-violet light has to be sent through a reflector and through the objective, fluorescence occurs on the objective itself, and as a result the light reflected from the back of the objective all over the tube—the actual visible light due to that fluorescence—became very serious in its actinic effect on the photographic plate, and I felt the only possibility of proceeding at all would be if a filter could be obtained which would exclude visible light and transmit the ultra-violet light almost undiminished. Prof. R. W. Wood, of Baltimore, suggested the silvering of one of the lenses, but that increased the exposure so enormously that it was hopeless. Other circumstances arose, and the matter had to be left aside. I hope someone may succeed in overcoming these difficulties, but I am not sanguine of the results which can be obtained with any kind of invisible radiation, and my reason is that such methods will only yield photographs. Photographs are extremely useful as a record of what you have seen, but as a means of actual microscopic examination they are not satisfactory. I always think it is necessary to examine successively large areas, and that you cannot, by using a few photographs of small areas, form a really good opinion.

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There is one other direction in which I think that higher resolving power is at any rate conceivable. Resolving power is a function of the numerical aperture expressed in terms of $u \sin a$. $\sin a$ cannot be increased very much, but what about u? The immersion liquid is a difficulty, but I think that a higher refractive index for the front glass is at any rate a thing where there is hope of success as the result of research. I agree with Sir Herbert Jackson that research will make it possible to make glasses of almost any desired kind; there is, however, a good deal of emphasis to be placed on the "almost," because the range of possible glasses is strictly confined within certain limits of refractive index. I have on a previous occasion given the values of these limits, and the limitation is due apparently to quite definite physical and chemical causes. Glasses having very low refractive indices or high ones, and having abnormal optical properties, are virulent chemical agents in their action on everything they may come in contact with, including air. They are rapidly attacked by moist air, and they crystallise during manufacture. There, I think, lies the solution of the problem. When we look for substances which have high refractive indices, we find them in crystals, and I want to carry that suggestion one step further. I made it many years ago, but with the renewed stimulus to research in this direction, it is worth making it again. The time has surely come when we should meet this question of crystalline substances for optical purposes by attempting to grow crystals artificially. I am quite sure that it can be done, and it ought to be done. I have made a few preliminary experiments of that kind, and have succeeded in producing some small calcium carbonate crystals. They were small, but they were large enough for short-focus lenses, and I think the idea of growing crystals is not altogether out of the range of practical possibilities to-day.

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THE METALLURGICAL MICROSCOPE.

By Walter Rosenhain, D.Sc., F.R.S.

(The National Physical Laboratory.)

In a paper* presented to the Royal Microscopical Society in 1906, the present author has described a Metallurgical Microscope in the design and construction of which an effort has been made to apply certain principles which he regards as fundamental for the construction of scientific instruments in general and of microscopes in particular. These principles have previously been discussed in a paper† presented to the Optical Convention, 1905. For the purposes of the present discussion, therefore, it will not be necessary to do more than to summarise briefly some of the principal points affecting the metallurgical microscope.

In regard to mechanical design, the primary consideration is that of providing adequate strength and stiffness not only in the base and limb, but also in the working joints, such as that upon which the limb turns. The design of such an instrument should, in fact, in the author's opinion, be based rather upon that of a machine tool than on the unduly delicate, sometimes flimsy, and often unmechanical devices which are to be found in some scientific instruments. One fruitful source of lack of rigidity may be found in the presence of unnecessary movements; for instance, it is now fairly generally accepted as an essential feature of metallurgical microscopes that the focussing movement, at all events so far as the coarse adjustment is concerned, should be applied to the stage. The provision of a coarse focussing movement for the body tube as well, therefore, constitutes an undesirable duplication. If the fine adjustment is also applied to the stage, as has been done in the author's design, then the body tube can be rigidly attached to the limb, with a corresponding gain in rigidity.

Another source of unsteadiness lies in the manner in which the so-called vertical illuminator is frequently attached. Where this fitting is screwed to the nose-end of the body tube and the objective is screwed into the illuminator, a certain amount of play is liable to occur. The author, therefore, very much prefers an arrangement by which the objective is screwed direct to the body tube, and the illuminator is inserted into the body tube, by means of a slide or otherwise, through a lateral aperture.

The application of the fine focussing adjustment to the stage offers a further advantage which is of some importance, as by this arrangement the fine focussing movement can be placed in an axial position. If this is done there is no overhang to magnify the slight play which is unavoidable on all smooth running slides. This

* "On an Improved Form of Metallurgical Microscope," Journal Royal Microscopical Society, 1906.

† "The Mechanical Design of Instruments," Proc. Optical Convention, Vol. 1, 1905.

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difficulty might perhaps be overcome in another way by adopting geometrical contacts instead of plain sliding contacts. The advantage of this system has long been recognised in theory, but instrument makers do not appear to have seen their way to its adoption on any large scale.

The illuminator and its adjustments deserve a little further consideration. Both for visual and photographic purposes the author has found it a very great advantage to have an illuminator whose position is capable of a very considerable range of adjustment. Whatever form of reflector be employed, it is always an advantage to be able to adjust its position not merely by rotation but by lateral and longitudinal movement in the tube. This is important, not only for the purpose of securing illumination at the precise incidence best suited for showing any particular feature, but also for the purpose of eliminating that most fruitful source of difficulties—internal reflections from the lenses of the objective.

Two further features of the mechanical design are of some importance. The first of these is the provision for a large working distance between stage and objectives. This is necessary not only to provide for the examination of thick specimens, but also because for many purposes the use of long focus objectives is necessary. This latter aspect of metallurgical work is assuming increasing importance at the present time owing to the fact that the study of macro-structures is now demanding much greater attention. In many cases these macro-structures are large enough to be photographed with an ordinary camera or even to be reproduced by means of direct contact printing. There are, however, many conditions in which the macro-structure is still sufficiently small to require magnifications of from 2 to 10 diameters, and it is very convenient for those who are not in a position to set up a separate apparatus for this purpose if their metallurgical microscope is capable of being used with long focus objectives working either with or without an eye-piece.

Another matter of some convenience in the metallurgical microscope is the provision of a complete rotation of the stage together with a simple centering device attached either to the stage or to the nose-end of the body tube. Rotation of the specimen is important for two reasons:—In the first place under oblique illumination the aspect of an etched surface varies in a most instructive manner with varying incidence of the light, and it is sometimes convenient to apply coloured illumination from two or more directions, and to be able to rotate the specimens under such illumination. In the second place, when a vertical illuminator is used which covers one-half of the aperture of the objectives, the resolving power is much greater in the direction parallel to the edge of the illuminator than in the direction at right angles to it.

Consequently in examining such a structure as finely laminated pearlite, this may appear uniform or " sorbitic " when viewed in the one position, while it becomes clearly resolved into laminae when turned through a right angle. This, of course, applies mainly to work at high magnifications under lenses of large resolving power.

Turning to the optical equipment of the metallurgical microscope, there can be no question that the requirements of metallurgy demand the best and even more than the best that optical achievements can

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provide. The requirements themselves are mainly those common to all microscopic work of the most exacting kind. In regard to the provision of the most critical definition, the highest possible resolving power and the largest and flattest field, together with the greatest possible approach to freedom from colour and the elimination of differences of actinic and visual focus, hitherto the best appo-chromatic lenses have provided the nearest approach to a fulfilment of these requirements. Metallurgical progress, however, undoubtedly tends increasingly to the production of materials having an extremely minute micro-structure, and the differentiation of these and the reading of their life history from their structure, makes increasing demands upon the resolving power of our lenses. The provision of a resolving power which should allow the employment of a much higher useful magnification becomes, therefore, of very considerable practical importance. Whether or not such an achievement is within the range of possibility is a matter for the optician rather than the metallurgist. The difficulties of the problem must, however, be very fully recognised; one of the most important, no doubt, resides in the difficulty of finding an immersion liquid, of very much higher refractive index than the cedar-wood oil commonly employed. The use of monobromonaphthalene immersion objectives has been tried, but they do not appear to have achieved any widespread use. An effort has also been made to meet this requirement by the use of light of much shorter wave-length. The author has spent a considerable amount of time in endeavouring to use the Zeiss ultra-violet microscope for metallurgical purposes, and has succeeded in obtaining a few micrographs by this means. He has, however, abandoned his efforts, because the expenditure of time required was much too great, while the results themselves were not particularly satisfactory. One of the main difficulties in his experience arose from the internal scattering of the ultra-violet light and the occurrence of fluorescence within the microscope tube. Even should it be possible to overcome these difficulties, a process which is entirely photographic, and in which the systematic visual examination of relatively large area of specimens is impossible, does not promise a very large range of utility.

Reverting to the requirements for objectives of the ordinary type intended for metallurgical use, there is one point which requires special emphasis and attention. Clear images, whether visual or photographic, can only be obtained if serious reflections of light from the back surface of the objectives can be avoided. As has been indicated above, this is partly a question of careful adjustment of the light and of the illuminator. With the best of facilities in that direction, however, the author's experience has shown very clearly that different lenses of the same focal length differ very widely in respect of this matter of internal reflections. This appears to be a question of the shape of the back lens of the objective, and especially of the outer surface. Where this is plane it appears to be possible to catch the whole of the reflected light on the mirror or prism of the illuminator, but where the back surface is convex this becomes impossible, and a milky image is very apt to result.

In regard to eye-piece requirements for metallurgical work, these do not appear to differ from those of other microscopical purposes; there is, however, from the user's point of view, a distinct objection

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to the use of eye-pieces such as the compensating eye-piece of Zeiss, which can only be used with a particular series of objectives. Unless, therefore, such an arrangement is really essential to allow the best results to be obtained, it will be very much preferable to have eye-pieces and objectives self-contained and interchangeable, not only with other lenses of the same series, but as nearly as may be universally. It may be desirable to state from the author's practice and experience the most useful focal lengths for objectives and magnifications for eye-pieces. It should perhaps be said that it is not suggested that any rigid standardisation of magnifications should be adopted by metallurgists. While a certain degree of uniformity of practice and especially the avoidance of odd magnifications are no doubt desirable, any attempt to tie down microscopists to a few specified magnifications is eminently undesirable, since the magnification for each subject should be chosen specifically to suit that subject. A range of objectives and eye-pieces is, therefore, in the author's opinion, desirable, which will allow of almost any desired magnifications being obtained in a satisfactory manner, that is, by use of an objective of adequately resolving power and without employing a high eye-piece or an unduly extended camera, where photographs are concerned.

The lenses ordinarily used by the author have focal lengths of:—

16 mm.
8 mm. } dry series.
4 mm.

2 mm.
3 mm. } oil immersion.

Eye-pieces—×8, ×12, ×18.

These lenses have been used because they have been commercially available in those makes which have in the past produced the finest results. So far as the objectives of the dry series are concerned, the focal lengths stated fulfil all ordinary requirements, although a 4 mm. dry objective is not easy to use and requires a great deal of stopping down of the beam of incident light. For this reason, the author, some time ago, suggested the desirability of an immersion lens of from 5 to 7 mm. focus. This would have the great advantage of affording a greater depth of focus than the 4 mm. dry objective, but it might prove difficult to use in a horizontal position unless a special device were provided for holding the oil in place.

With regard to the immersion objectives, that which has given the finest results for the highest magnifications in the author's practice, has been a lens of 3 mm. focus with N.A. 1.40. Unfortunately, these lenses are very delicate in use, and require not only protection from mechanical injury, but also from any agency which affects the cement with which the front lens is attached to the mount and from prolonged exposure to contact with immersion oil. If the latter is not of precisely the right quality, this is alone sufficient to do damage. If this oil is wiped away very gently with a soft cloth and the surface of the lens is then wiped lightly with an old handkerchief slightly moistened with benzol, damage to the cement may be avoided for a long time.

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Beyond the objectives named above, a demand exists, and is becoming increasingly important, as indicated above, for first-class objectives of long focus. The author would welcome such objectives having focal lengths of 30 mm., 50 mm. and 75 mm., suitable mainly for photographic purposes. It would, however, be an advantage if they could be designed to work with a low power eye-piece so that they could also be used for visual work.

The accessories required in metallurgical microscopy are of some importance. A satisfactory illuminant is essential to all good work of this kind. For visual purposes, the requirements are easily met,

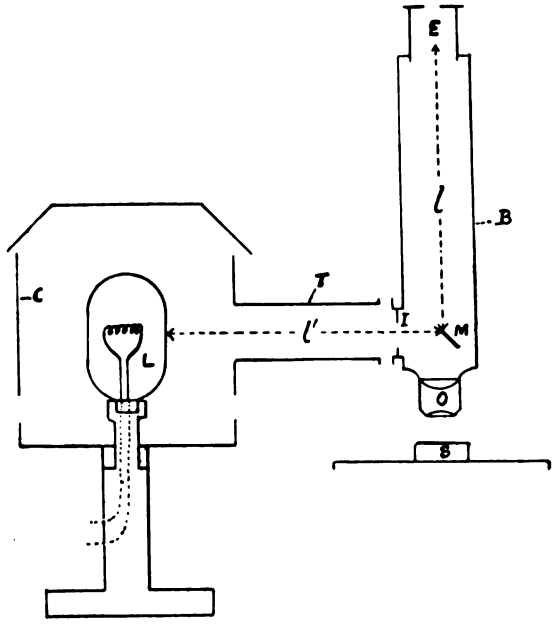

FIG. 1.

since it is only necessary to place opposite to the lateral aperture of the illuminator an uniform source of light having a reasonable area (about 2 centimetres in diameter). Such a source of light may be obtained by placing a suitable burner or electric lamp behind either very finely ground glass or a thin piece of opal shade. If the luminous surface thus produced is placed to one side of the microscope in such a position that its distance from the illuminator mirror is equal to the distance from that mirror to the back focus of the objective, the result is an approach to the conditions of "critical illumination," and for visual purposes these are certainly the best conditions obtainable. This arrangement has the further advantage that no lenses, condensers, etc., are required, and that an iris diaphragm placed just outside the illuminator aperture is all that is needed to regulate the illumination. The whole arrangement can be very simply made by mounting the lamp with a short external tube through which the light passes to the illuminator, the rest of

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the lamp being enclosed in a light, tight, but suitably ventilated, case. If the lateral tube through which the light passes is made of the right length, all that is necessary for setting up the illuminating arrangement is to switch on the lamp and to place the small tube almost but not quite in contact with the rim of the iris diaphragm outside the illuminator. A diagrammatic section of this whole arrangement is given in Fig. 1, and a photograph is shown in Fig. 2.

For photographic purposes, the intensity of the illumination obtainable in this way is not large enough to be convenient. The author has endeavoured to use one of the small tungsten arc-lamps known as "Pointolite," as the source for critical illumination in photography, by placing the lamp itself in the conjugate focus position. But with the largest size of this type of lamp at present available, the illuminated area is not large enough. It is to be hoped, however, that a larger form of this lamp may become available, and in that case it will be possible to carry out the best kind of micrographic work without the use of a system of condensers, such as are employed at present.

The arrangements for fine focussing of the microscope when used for photographic purposes frequently present imperfections which are annoying in use, and are liable to lead to the loss of photographic material. Whether gearing or a cord serving as a belt are employed, there is always apt to be some degree of lateral pull applied to the microscope when the fine adjustment head is turned by the operator working from the screen end of the camera. The author has devised a very simple means of avoiding this difficulty and of leaving the microscope free as soon as the operator's touch is removed from the focussing rod. For this purpose, the focussing rod, extending along the length of the camera, operates by means of a small belt, a rotating spindle attached to an independent bearing carries on a separate stand. This rotating spindle is so placed as to be axial with the fine adjustment of the microscope, in whatever position this may be situated. The end of the spindle nearest the microscope merely carries a cross-piece consisting of a thin rod. Fixed to the fine adjustment head of the microscope itself is a light tube of brass or aluminium. In this tube are two longitudinal slots diametrically opposite one another. The independent spindle above mentioned runs down the axis of this tube, but the transverse rod has its ends projecting through the slots of the tube, the slots being made a little wider than the diameter of the rod. If now the spindle is rotated by the operator turning the focussing handle, no pull whatever is placed upon the fine adjustment of the microscope—the motion of the spindle being transmitted to the fine adjustment through the slots in the tube. In these circumstances, a pure turning moment or torque is applied to the fine adjustment, so that there is no tendency to displace the microscope. Further, if the belt connecting the focussing handle to the moving spindle is slightly elastic, the moment the pressure of the operator's hand is removed from the focussing handle, the spindle and the transverse rod which it carries will spring back by a very small amount. In this way, the rod is brought out of contact with the tube, and the microscope is left entirely free from contact with the focussing gear.

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If the fine adjustment of the microscope is of the ordinary type in which the head has only a very small longitudinal motion, the tube, slots, and spindle mentioned above also need only be very short. On the other hand, in the type of microscope designed by the author, in which the fine adjustment may be moved through considerable distance by the coarse focussing of the stage, the tube, slots, and spindle must have a length of several inches. This focussing device, which is somewhat difficult to describe in words, is very simple and efficient in action. It is illustrated in the photograph, Fig. 3.

Finally, reference may be made to another matter which sometimes gives difficulty in metallurgical microscopy. This is the mounting of specimens with their surfaces accurately at right angles to the optic axis of the microscope. Mechanical levelling devices of various kinds have proved more or less successful, but they all have the serious disadvantage that the carefully prepared surface of the specimen must be placed in contact with some part of the apparatus, and when this is done there is considerable risk of damaging the surface. The author, therefore, has devised an optical levelling appliance in which the surface of the specimen is utilised as a reflector. The specimen is approximately mounted on a glass slip by means of plasticine, wax or other soft substance. It is then placed under the instrument, and its position is adjusted with the fingers until the reflection is seen opposite a cross-wire. When this position has been obtained, the specimen is accurately level, and the manipulation is so easy that it rarely occupies more than five seconds. A more detailed description of this device has been given in the author's paper on "Some Appliances for Metallographic Research."*

* Journ. Institute of Metals, 1915, I.

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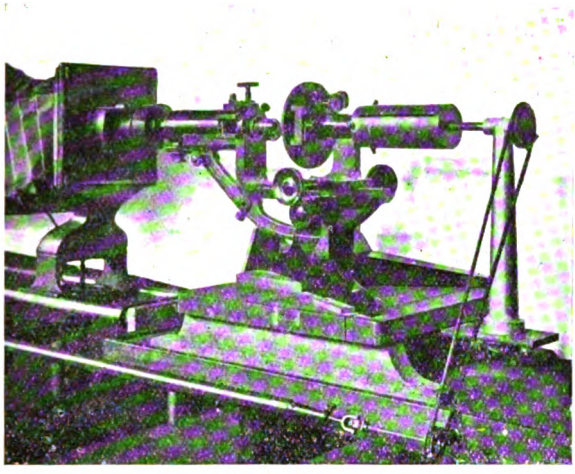

FIG. 2.
Independent Focussing Device applied to Metallurgical Microscope as used for Photography.

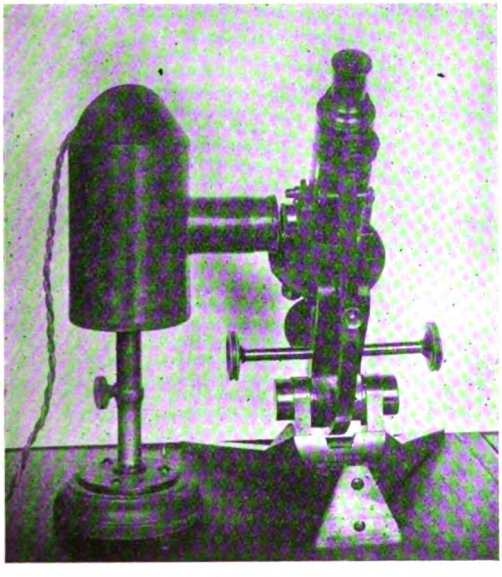

FIG. 3.

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NOTES ON THE CONSTRUCTION AND DESIGN OF METALLURGICAL MICROSCOPES.

By Prof. Cecil H. Desch, Glasgow.

The use of the microscope in the examination of metals, first introduced by Sorby more than 50 years ago, has become so widespread that a microscope is now an indispensable item in the equipment of a metallurgical works, whilst the recognition of its importance to engineering works and other places in which metals are employed for constructional purposes is rapidly extending. It is therefore essential to the conduct of these industries that instruments should be available which will allow of the rapid and convenient examination of such metals as present themselves in the course of routine testing, whilst it is obviously desirable that elaborate and detailed investigation of specimens of special interest should be possible. It is quite true that any ordinary microscope of good construction may be used for metallographic work, provided that the higher power objectives are duly corrected for uncovered objects, but the increased convenience of a properly designed instrument is so great as to justify its use, even for routine work. There are now many patterns of metallurgical microscopes on the market, and the following remarks are based on an experience of some 12 or 13 types of instrument, and the examination of the details of many others. The writer has been reluctantly forced to the conclusion that, in spite of many excellent features in some of the British microscopes, the German instruments have proved better in use, and that their superiority is more marked, the longer the microscopes are used. The British designs are often good, and the workmanship, so far as the cutting of racks and screw-threads, etc., is concerned, is often quite satisfactory, but in the course of prolonged use the mechanical arrangements show defects, racks and screws becoming loose, and the accurate focussing of high power objectives becoming troublesome, to an extent which is not met with in the German microscopes. The cause of this looseness after use appears to be insufficient attention to the quality of the metal employed in construction. A rack cut in soft brass, however accurate at first, becomes loose through wear, and no compensation by means of adjusting screws can be quite satisfactory. The fact that such screws are provided seems to be a confession of weakness, since the writer has used a Zeiss microscope, without such screws, for years continuously without any sign of play in the mechanical movements. Racks should be cut in hard, incorrodible metals or alloys instead of in soft brass, whilst the pinions might also be of much harder metal than is usually the case. It is probable that manufacturers have been too much guided by tradition in the choice of the metals to be used in the construction of scientific instruments, witness the tendency, only now disappearing, to use highly polished brass for heavy portions where cast iron would serve the purpose equally well.

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The principal parts of the metallurgical microscope may now be considered in succession.

(a) *The Stand.*—There is no reason why the shape of the medical or biological microscope should be slavishly copied in the construction of metallurgical instruments, whilst there are many reasons for choosing a different form, especially when there is a possibility of large specimens being examined. The tripod form of foot, so convenient in work by transmitted light, is awkwardly in the way when examining metals and having occasion to use the rackwork movement for raising and lowering the stage. The Jackson foot is better, and a heavy horseshoe foot still better, as heavy specimens, such as rail sections, may be laid on it for examination under low powers. This is further facilitated by making the bracket which holds the stage capable of swinging to one side, and leaving a clear space between the objective and the heavy horseshoe foot, as in the old vertical Reichert microscope. Special forms of foot, as in the Beck-Rosenhain microscope, have the advantage of great rigidity in both the vertical and horizontal positions. This stand is the most rigid of those examined. The design of Sauveur's universal Metalloscope is also unconventional, and appears to be good, but the writer has no actual experience of it. For photographic work the form adopted in the Zeiss-Martens instrument and in Watson's horizontal microscope is both convenient and steady.

The inverted stand, due to Le Chatelier, has been copied by several makers, but the construction is apt to be flimsy, and the writer has found great difficulty in moving even small specimens on the stage without altering the focus, the light arms which support the optical parts being liable to whip. This could perhaps be overcome by better engineering design, and the type is certainly preferred in some works on account of the rapidity with which specimens can be inserted and examined. The optical conditions of this form are discussed below. It is probable that for the larger instruments to be used for photography the ordinary type of stand might be departed from entirely, and an arrangement modelled on the optical bench adopted, the various optical parts and specimen carriers being supported in such a way as to move freely along a heavy bar of geometrical form to preserve alignment.

(b) *Course Adjustment.*—The rack and pinion should be geometrically cut in metal of sufficient hardness to withstand prolonged usage without working loose. The improvement in the methods of gear cutting in engineering practice has been so great in recent years that much would be gained by adopting the methods of marine engineering shops in the instrument maker's workshop. In large instruments, the length of travel might well be greater than at present, so as to allow of a wide range of objectives, and stops should be provided at the ends of the rack to prevent over-

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racking. This is particularly desirable in students' microscopes, as it would prevent a common accident in laboratories where inexperienced students use the instruments.

(c) *Fine Adjustment.*—This does not call for much remark, as there are several good forms in use. The speed is sometimes made too great for comfortable focussing of high powers. The side arrangement of small milled heads is perhaps the most convenient.

(d) *Body Tube.*—This should be of the short Continental form, and preferably of wide diameter. The latter condition is essential in instruments to be used for photographic work, and should always be adopted, but it has also great advantages for visual observation, and can be introduced without interfering with the general design.

(e) *The Stage.*—A plain stage of fairly large size is suitable for most ordinary work. It should be provided with a rackwork focussing movement, but a fine adjustment is unnecessary. A central hole, sufficiently large to allow an objective to pass through it, allows of the examination of heavy specimens resting on the foot, unless the support of the stage be arranged to swing aside entirely, as mentioned above. Levelling stages are a nuisance, and should never be used. The specimen should always be levelled before placing on the stage, either by means of plasticine and one of the usual mounting devices, or by means of Dr. Rosenhain's auto-collimating instrument. Mechanical movements to the stage are essential for high power work, and rotation is also a very great convenience, but when both are provided the rotation should be concentric. A rotating plate which is carried by the traversing movements is useless. When a microscope is intended to be used in the horizontal position, it is desirable to provide the mechanical movements with clamping screws, as otherwise a heavy specimen may cause a gradual downward slip during the exposure of a photograph, pulling down the rackwork by its own weight. This has often been noticed when photographing at high magnifications. The rotating circle should have a clamping screw. The Zeiss-Martens stand has a very convenient rotating and traversing stage, but the range of movement is too limited.

The examination of fractures, large crystals in ingot sections, and other things requiring very low powers and great distances, is troublesome when an ordinary microscope is used, and it is often preferable to employ a camera with a landscape or copying lens instead of a microscope. The telephoto attachment of the Davidson microscope gives good results in this kind of work, and the arrangement in the recent pattern, by which the object is carried on a separate stand, movable along a base board, is convenient. On the other hand, the writer does not approve

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of the "super-microscope" arrangement, by which the image formed by one objective is magnified by a second objective.

(f) *The Vertical Illuminator.*—Whilst the prism form has the advantage for visual work of causing much less loss of light than the transparent plate, it is unsuitable for high powers, on account of the fact that it only uses one-half of the aperture of the objective, and is consequently liable to produce false images of fine structures. The same objection applies to silvered half-discs or other similar devices. The Beck or transparent illuminator is the only suitable form for photographic work at any but low magnifications. The mistake is very commonly made of fitting a small cover glass, which only imperfectly covers the back lens of the objective, into such illuminators. A plate of larger size should be used. Moreover, cover glasses are not accurately flat, and have no advantage except cheapness and thinness. A large, optically worked plate is used in the Conrady-Watson illuminator and in the Jackson and Blount microscope. The writer has found the thin, square plates used for counting blood corpuscles very suitable, being sufficiently flat and so thin as not to produce doubling of the image. The plate should be capable of at least partial rotation, and should have a sufficiently large milled head to allow of delicate adjustment. Vertical illuminators often leave much to be desired in regard to mechanical construction.

The inverted or Le Chatelier type of microscope calls for a different form of illuminator. As usually constructed, the numerous reflections required tend to injure the definition of the image and to cause loss of light. To a great extent this might be obviated by better optical workmanship, the prism being made in one piece with accurately ground faces, as in the modern range finder. The possibilities of new optical arrangements for illumination are not exhausted.

(g) *The Objectives.*—It is now generally agreed that short mounts are to be preferred for metallographic objectives. A high numerical aperture is necessary for the highest powers. Apochromats are usually recommended for the medium and high powers, but such objectives are commonly deficient in flatness of field, a very desirable quality in metallographic work, and it may be questioned whether good achromats, giving flat fields, are not to be preferred for photographic purposes. It is usual to insert a colour screen when making such photographs, and now that screens which transmit so narrow a band of the spectrum that they may be regarded as practically monochromatic are obtainable, it seems of less importance that the colour correction of the objectives should be perfect. Oil immersion objectives are, of course, necessary for the highest magnifications.

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(h) *Eye-pieces.*—These give the least trouble of all the parts of the microscope, the quality being usually satisfactory. Projection eye-pieces are to be preferred for photographic work.

These few notes are presented by way of suggestions for discussion. Each worker will have formed some opinion on the points mentioned, and a comparison of such opinions may be of assistance to manufacturers in determining the design of their future instruments. There is a large demand for metallographic microscopes at present, whilst the supply is very limited, and the time seems appropriate for a consideration of the question whether improvements might not be made in the light of experience.

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SOME NOTES ON THE METALLURGICAL PHOTOMICROSCOPE.

By J. H. G. Monypenny.

(Chief of the Research Laboratory, Brown Bayley's Steel Works, Ltd.)

The technique of the photomicrography of metals has advanced very much during the last ten or twenty years, but there are still very marked evidences that many who take up microscopic work in connection with metallurgy appear to study the microscope itself either not at all or only to a very small extent. The consequence is that statements are made about the structures of various metals which are not correct; the presence in sections of minute particles or membranes of constituents other than those stated to be there has been missed simply because the operator did not know how to use his microscope properly. Again, photographs are published which have only a slight resemblance to the structures photographed, in some cases the definition is so bad that the reproductions are not worth the paper they are printed upon. One has only to look through the Journals of, for example, the Iron and Steel Institute to see how true this is.

Even when a metallurgist has devoted a considerable time to the study of the microscope, mistakes may arise in the interpretation of structures. For example, it has been stated that iron carbide (cementite) is not attacked by sodium picrate when its thickness is less than 0.001 mm. (this statement is repeated in one of the most recently published treatises on metallography). This is quite incorrect. Not only are the carbide laminae of pearlite attacked when considerably thinner than this (certainly not more than one-tenth of the thickness mentioned), but also the minute granules in sorbite, produced on tempering hardened steel at about 600° C. Possibly the reason the above misstatement was originally made was either that the aperture of the objective used was not sufficiently high or that the resolving power was much reduced by the use of a prism illuminator or both.

In the following pages the author has attempted to set out some of the conditions which appear to him to be necessary to secure good photomicrographs of metals and the means he has devised from time to time to fulfil these conditions.

(a) *The Illuminant and Condensing System.*—Few who have had any experience in photomicrography will disagree with the statement that the illumination of the specimen is of fundamental importance in the production of a good photomicrograph. Good illumination should comply with the four following conditions:—

(1) The whole surface which is required to be reproduced should be evenly illuminated.

(2) The lighting should be such that the whole aperture of the objective may be utilised.

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(3) The wave-length of the light used should be that for which the objective is corrected.

(4) The wave-length of the light used should be suitable to the colour of the specimen.

Fortunately, in most metallurgical work the specimens rarely call for the use of any definite colour of light, and hence the necessity for complying with condition No. 4 does not, in general, arise. This is a great advantage, as it enables one to adjust the colour of the light to fulfil condition (3). In other branches of microscopic work (*e.g.*, in connection with Biology), it may easily occur that the requirements under conditions (3) and (4) are opposite, and then the photomicrographer has either to use a colour for which the objective is not adequately corrected or which is not best suited to the specimen.

In metallurgical work the objective acts as condenser, and it is well known that to produce " critical illumination " the illuminant should be focussed on the section, and should therefore occupy the

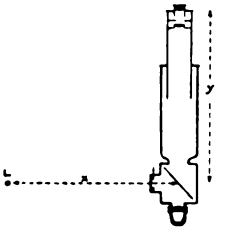

FIG. 1.

Diagram showing conditions for critical illumination.

position L shown in Fig. 1, so that the distances x and y are equal. Practically it is found that the illuminant may be to some extent out of focus without producing any bad effect, providing the objective transmits a full solid cone of light. This may be judged by looking at the back lens of the objective after removing the eye-piece, when (the iris on the vertical illuminator being open) the back lens will be full of light and evenly bright if critical illumination has been obtained. The fact that the illuminant may be to some extent out of focus is of great value in allowing one to get rid of the effect of small surface markings on the illuminant itself.

Placing the illuminant in such a position has obvious disadvantages, *e.g.*, it would be inconveniently close to the microscope and the heating effect produced on the latter would be considerable. Again, to illuminate the whole visible field in the microscope, the illuminant would have to have an evenly bright area at least as large as the diaphragm of the ocular in use (say 7 to 8 mm.), obviously, therefore, illuminants of small area (*e.g.*, Nernst or Arc lamps) could not be used in this way.

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As regards the illuminant, the author prefers the 500 C.P. Pointolite Lamp (a tungsten arc lamp made by the Ediswan Co.) to any other type of lamp made; the intensity of the light is very great, and it is absolutely steady. It requires direct current, and where this is available the author has no hesitation whatever in recommending it in preference to any other form of illuminant. Previous to this lamp being on the market (about 1917), the author had tried a Nernst lamp, an arc lamp, and lime-light, and had for some years used the last in preference to the first two. The intensity of the light given by the lime is not nearly so great as with the arc lamp, but on the other hand it is perfectly steady, and this cannot be said of the arc lamp.

Coming to the condensing system, probably one of the simplest arrangements is that shown in Fig. 2. In this case the condenser C forms an enlarged image of the illuminant L at L_1, the correct distance from the illuminator to give critical illumination as described earlier. By this means the area of the illuminant is spread out, and with, for example, lime-light, one may obtain perfectly even illumination even when photographing at, say, 5 or 6 times the initial power of the objective. The effect of any slight irregularities

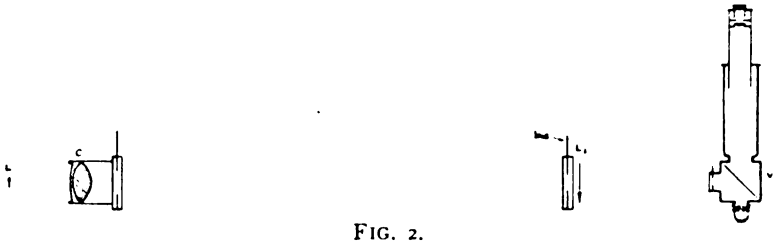

FIG. 2.
Condenser System No. 1.

on the surface of the illuminant may be avoided by forming the image L_1 about 1 in. nearer the microscope than its correct position, as mentioned earlier. It is advisable to have an iris diaphragm at L_1 and to close it until only slightly more than the area to be photographed is illuminated. This cuts off a lot of stray light which would otherwise reduce the contrast by giving a general fog over the whole section. This iris should be focussed fairly accurately on the section, otherwise there is a gradual falling off of the illumination on the edge of the field instead of a sharply defined edge to the illuminated area.

While this method is perfectly satisfactory for use with lime-light —the author has taken several hundred photographs at magnifications ranging from 30 to 2,000, using an arrangement of this description—it has certain drawbacks; for example, a great deal of light is wasted, and with an illuminant of small area it is difficult to fill the field evenly unless a very long optical bench is used.

These defects are obviated in the following arrangement. In this, advantage is taken of the fact that if a biconvex lens is held between the eye and a light (*e.g.*, a candle flame) in such a manner that the eye and flame occupy the position of conjugate foci then the lens itself will appear to the eye as an evenly illuminated disc, and

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for the purposes of microscopic work may be looked upon as an illuminant. There is one essential point, however, the beam of light thrown by the lens must cover the whole surface of the back lens of the objective, otherwise some of the aperture of the latter is lost.

In Fig. 3, A represents a lens of about 6 in. focus, placed at the requisite distance from the microscope to give critical illumination, as described earlier; the objective therefore uses this lens as the illuminant, and forms an image of it in the field (if any slight scratches are present on the surface of the lens, it should be moved very slightly out of focus). Condenser B (about 2⅝ in. focus and 2⅛ in. diameter) is placed at such a distance from A that the

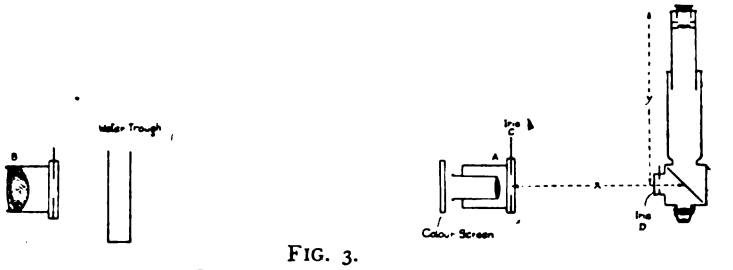

FIG. 3.
Condenser System No. 2.

latter focusses B approximately on the objective. Finally B forms an enlarged image of the illuminant on A. This sounds rather complex, but the result is that if the eye be placed at A, B appears as an even disc of light, and similarly to an eye placed against the objective A appears as an even disc. As mentioned above, the only point that must be carefully watched is that the image of B formed by A on the objective must at least cover the back lens of the latter. The figures given above refer to the author's arrangement, and in this case the image is rather more than two-thirds of an inch diameter, and therefore amply large enough for any objective in use. Condenser A need not be more than 1 in. diameter, but the image of the light formed on this lens by B should completely fill it. This condenser (A) should have an iris diaphragm for limiting the area of the field illuminated as described earlier. An iris is not required on condenser B, except for centering and focussing purposes.

Using this arrangement, one is able to illuminate evenly the section, and also provide critical illumination. It will be found that if condenser A is used without B, unless the illuminant has a large area or is placed very near to A, the conditions of critical illumination are not obtained, the beam of light not being sufficient to fill the back lens of the objective. The effect is equivalent to cutting down the aperture of the objective, with all the bad effects produced thereby. The author has seen more than one metallurgical photomicroscope in use in which this condition of things has obtained.

It is obvious from Fig. 3 that, using an illuminant of small area, such as the Pointolite, condenser B should have a short focus, and also the better corrected it is the more light will be available—the author uses the Watson-Conrady condenser, and finds it excellent

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for the purpose. Doubtless other opticians could supply similarly corrected condensers. Condenser A has a longer focus (the actual focal length will depend on the tube length employed and the distance between the condensers), and as it need only be of small diameter, such a high degree of correction as in B does not seem necessary.

(b) *The Vertical Illuminator.*—The author does not propose to enter into the question of prism *versus* disc illuminator to any great extent. The fact that with high powers a disc illuminator must of necessity give and does give far better definition and much more detail, is evident to anyone who has studied the subject or who has critically compared the two illuminators with the same lens on the same field. Examples of this have been published independently by Rosenhain and by Benedicks; the author (who was unaware of Rosenhain's work) investigated the matter before Benedicks' paper was published, and his results, though not published, were communicated to some of his friends. It is probably not so well known, however, that the results with low power lenses show the same differences, though not in so marked a manner. The differences produced for any given objective depend on the fineness of detail in the section. Other things being equal, the superiority of the disc becomes more marked as the detail to be reproduced becomes finer. The author always uses a disc illuminator even with the lowest powers, except under exceptional circumstances. (Such may arise in a low power photograph of an object showing no fine detail and possessing very little contrast.)

While, however, the author is convinced of the superiority of the disc illuminator, he has found that many individual discs are very poor specimens, and in this respect he would urge on instrument makers the necessity for more care in choosing material for the "disc." In many cases the glass is so thick and so uneven that the definition of even a low power lens in absolutely ruined. The author a few years ago received an illuminator from one of the largest microscope makers in England—he returned it at once with a note that it was useless owing to the bad glass (giving them details of the behaviour of the disc). The illuminator was returned to him with a fresh glass fitted, which was every bit as bad as the first one. The effect of this bad disc is shown in Figs. 4 and 5. These represent the same field taken with the same objective, ocular, plate, and screen, in fact every condition the same, except that in Fig. 4 the disc was a good one, while in Fig. 5 the disc was the bad one mentioned above. It was absolutely impossible to get any sharper definition than that shown in Fig. 5. The author suggests that this is a point to which instrument makers should give far more attention than they do—there is no doubt at all that many of the glasses supplied with disc illuminators are far too thick, and they are often uneven. It is evident also that the discs cannot be very carefully examined by the makers before being put into stock, otherwise such defects would be quickly discovered.

It may be of interest to mention that the bad disc mentioned above had far more effect on the performance of the 1 in. and ½ in. objectives than on the 1-6th, probably owing to the larger area of the glass used by the former lenses. Probably this fact and the

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prevalence of unsuitable material for the disc may account for the opinion frequently held that for such low powers the prism illuminator gives the better effect. A prism would give a much better result than Fig. 5.

There are three other points in connection with the vertical illuminator that the author would like to mention.

(1) The illuminator is rarely made large enough to fill the back lenses of the lower power objectives—for example, the 24 mm. N.A. .30 or the 12 mm. N.A. .65. The only disc illuminator known to the author which is large enough for these lenses is the large pattern made by Watsons, London.

(2) The illuminator should be fitted with an iris diaphragm, which should have some type of centering adjustment. This iris is used in the same manner as the iris on a substage condenser, and should therefore close absolutely central with the objective. Such adjusting movements as are found on the Watson pattern mentioned above are suitable.

In connection with the prism illuminator it is curious that in the pattern as ordinarily sold, the iris diaphragm closes concentrically with the middle of the front face of the prism, and therefore with a line about one-eighth of an inch from the centre line of the objective. The iris should, of course, close concentrically with the middle of the bottom edge of the prism, as shown in Fig. 6, where A indicates the centre line of the iris as ordinarily fitted, and B the line on which it should close. The effect, on the performance of an objective of short focal length, of closing the iris about line A can be imagined.

(3) One of the great defects of the disc illuminator, especially with the lower power objectives, is the presence of flare due to the reflection of the incident light by the outer surface of the back combination. This is a matter, however, which could probably be remedied to a great extent by the objective designer. It will be obvious that (other things being equal), the more convex this back surface is, the less the amount of flare, since more of the reflected light will be reflected on to the inner surface of the draw tube (and be absorbed by the blackened surface), and less will reach the eye-piece. The author has one lens in his possession in which the back surface is apparently slightly concave, and, owing to the amount of flare caused thereby, the lens, though a magnificent one from every other point of view (it is the Zeiss 12 mm. Apochromat N.A. .65) is not so valuable metallographically. The author would suggest that this is a point to which opticians could usefully give their attention in computing objectives for metallurgical work.

It is, of course, obvious that with the present method of construction of objectives there is much more likelihood of flare being obtained with apochromatic objectives than with achromatic—especially with the lower powers. In the former the back combination has very little magnifying power, its function being chiefly that of correcting the aberrations and other faults of the front combinations. In the simpler achromatic the back combination frequently has a considerable magnifying power. The more convex back surface of the latter type of lens will therefore cause less flare than the less convex surface of the more highly corrected combination. The author has frequently noticed this difference in

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comparing the different types of lenses. Very often the effect of the flare can be overcome by using a combination of plate and developer which gives contrast easily; for example, such methods succeed perfectly with the 24 mm. Zeiss apochromat; with the 12 mm., however, as stated above, the flare is so great that the author uses for preference a very good achromatic lens of the same aperture.

(c) *Colour Screens.*—As mentioned earlier in the paper, the use of colour screens in metallurgical work is simplified very much, as it is only on very rare occasions that a section is obtained which requires light of some definite wave-length in order to get the best results, consequently the whole attention can be given to using the light most suited to the lens.

If the objective is apochromatic, light of any colour may be used, but it is generally advisable to use blue light in preference to green or red (especially with the higher powers), as the resolving power is thereby increased. It is *always* advisable, however, even with the best apochromats, to focus with the same colour light as is used for photographing. The author's general practice in this case is to focus with a blue screen in position (generally the Wratten tricolour blue), and then remove the screen and expose on a non-colour sensitive plate (all blue screens increase the exposure rather considerably). This method is perfectly satisfactory for the Zeiss apochromats, even at the highest magnifications.

With achromatic, or semi-apochromatic lenses, one has not the same freedom. Owing to the simpler construction of these lenses the correction for spherical aberration is taken to a high degree of perfection for light of one colour only (generally yellow green), and the best results are only obtainable by using this colour. The author has examined such objectives made by most of the leading makers in England, and has never met one in which the correction for spherical aberration for blue violet light was sufficiently good (compared with that for green light) to make it worth while taking photographs with such light. Some lenses were certainly better than others, and, curiously enough, some of the lenses which were very poor with blue light worked quite well with red light. The author is of opinion that it would be far better if this fact were more widely acknowledged by the makers. To read the catalogue descriptions of some of the lenses one would imagine that they would perform perfectly without any screen at all. The author has known of cases where objectives by well-known English makers have been purchased and used in the belief that they would perform well under these conditions. After seeing the results the purchaser came to the conclusion that the lenses were very poor specimens. In one case which occurred recently the author was able to convince the purchaser that the type of lens in question would give very fine results if used with a suitable colour screen instead of in the manner suggested by reading the maker's too optimistic description. Probably one of the best screens to use for such lenses is one of the tricolour green type. The author uses the one made by Wratten, along with the Allochrome plate by the same maker. Such a plate as this (sensitive to yellow green) is preferable for this purpose to a panchromatic plate, as the red sensitiveness of the latter is no advantage—rather the reverse.

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(d) *The Relationship of Aperture and Magnification.*—With the author's arrangement of condensers, the beam of light entering the vertical illuminator is rather larger than the largest back lens of any objective he has; it is therefore necessary to use the iris diaphragm on the illuminator (D, Fig. 3). His practice is to cut down as little as possible. Generally he leaves the back combination 5-6ths full; it is only on rare occasions that he reduces below this. If the aperture is cut down much more than this, any surface irregularities due to scratches are shown up in a very prominent manner, owing to diffraction bands. For this reason, of course, it is well to reduce the aperture to less than 5-6ths when any relief effects in the structure have to be emphasised. The effect of gradually reducing the aperture of an objective has probably been studied mostly from the point of view of the higher power objectives. The bad effect produced on the images given by such lenses owing to such reduction is probably well known, though the fact that photomicrographs of metals showing diffraction effects caused by such reduction are still published shows that this bad effect is not always sufficiently appreciated. With lower power lenses the effects are not so marked metallurgically, since, generally, the photographs taken with such lenses give a general view over a large field, and are not intended to show fine detail. In addition to this, such low power lenses (*e.g.*, 1 in. or 2-3rds) have in general a higher ratio of N.A. to magnification than the higher powers. For example, the N.A. of the lenses mentioned above is generally between .24 and .30, and they are used for photographs at, say, 50 to 150 diameters. On the other hand, twelfths used at 1,000 and 1,500 diameters have at the most 1.4 N.A., and frequently only 1.2 to 1.3. Consequently there is more latitude with the stopping down of low power lenses, but still it should be remembered that with these lenses diffraction effects are produced, and there is a limit to the reduction of the aperture beyond which it is not advisable to go. By suitable stopping down, however, one can often, with these low powers, obtain a larger field sharp all over—frequently of great importance.

Under present conditions nothing is gained by photographing at any higher magnifications than about 1,500; with the present maximum aperture available (N.A. 1.40), all detail which can be shown is visible at this magnification. Any higher magnification is of the nature of an enlargement, and can be obtained equally as well by photographing at this magnification (×1,500), and enlarging from the negative, as by taking the negative direct at the higher magnification. There is no doubt that for many metallurgical purposes a higher magnification, coupled with greater resolving power, would be of great value. This could be obtained either by using light of very short wave-length, with its attendant difficulties of focussing, and also the necessity of special lenses capable of transmitting light of such short wave-length or by increasing the aperture of the objective. With regard to the latter, the author believes the firm of Zeiss produced some years ago a 2.5 mm. objective working at about N.A. 1.65. This objective had a front of flint glass, and used as immersion fluid monobromide of naphthaline. Its use, however, for transparent work was attended with great difficulties and expense, inasmuch as the slip and cover glass had

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to be of flint glass. With metallurgical work, however, these difficulties would not occur, and it seems to the author that such a lens would be of value in elucidating some of the finer structures met with in metals. If such a lens could be made it should preferably be apochromatic, but, if not, it might be advisable to correct it for blue violet, as the " preferred colour," in order that the highest resolving power could be obtained photographically.

It is obvious that at the highest powers the apochromatic lens has a much greater resolving power than the semi-apochromatic of the same aperture, owing to its capability of working with blue violet light. It should be emphasised that, other things being equal, using light of wave-length 4,500 A.U. instead of 5,500 A.U. is equivalent in its effects to increasing the N.A. approximately 25 per cent.

(e) *Exposure and Vibration Effects.*—In metallurgical photomicroscopes for use in works' laboratories it is very important that the exposure required, especially with high magnifications, should be as short as possible in order to avoid the effects of unavoidable vibrations. For such purposes an intense illuminant is required, and such lamps evolve a very considerable amount of heat, which may easily cause trouble with the cement used in the various combinations of the objective. It is very necessary in such cases that an adequate cooling trough be placed in the beam of light before it reaches the microscope. The heat evolved also causes trouble owing to the expansion effects produced in different parts of the microscope and camera.

Even when the exposures are comparatively short (*e.g.*, a few seconds), they still give plenty of time in the case of the higher powers for vibration to have considerable effect. The author has, however, been able to overcome this completely by swinging the whole photomicroscope on springs, as shown in Fig. 7. It will be noticed that the author's camera is vertical. This position has several advantages from a works' point of view; obviously it occupies less floor space than the horizontal pattern, and is probably more easily swung than the latter. It may be mentioned that, with the suspension system used, photographs at 1,000 and 1,500 diameters were successfully taken, although the laboratory was within 50 yards of four 8-ton steam hammers, and also adjoined three sets of railway lines running into the works.

(f) *Low Power Photography.*—It is frequently desirable to be able to reproduce at low magnifications fairly large areas under vertical illumination. With ordinary low power objectives (*e.g.*, 2 in. or 3 in.), it is possible to take photographs at, say, 20 or 30 diameters, but in general the field is only small, about $\frac{1}{8}$ in. or $\frac{1}{16}$ in. diameter. If attempts are made to get a larger field, trouble is at once experienced with the illumination, and often with the definition falling off. Frequently a very large field is required if the photograph is to serve its purpose, as, for example, with groups of flaws, very coarse structures, and segregated areas.

Some ten or twelve years ago the author devised an arrangement for this purpose, and as he has found it exceedingly useful, he puts it forward in the hope that it may be of use to others. There is nothing really novel in the method, it is a combination of several

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ideas, but so far as the author is aware, such an arrangement has not been described before, nor has he heard of any similar apparatus.

For such work the ordinary low power objective is not suitable—its "field" is not big enough. The lens the author uses is the 35 mm. projection lens made by Zeiss, though probably equally good results could be obtained with some of the very short focus photographic lenses made by various opticians. As illuminator he uses a piece of microscopic cover glass $1\frac{7}{8}$ in. × $1\frac{1}{4}$ in., mounted in a light brass frame which fits on to the objective. The frame is pivoted, allowing the illumination to be adjusted to a nicety. This disc is used between the objective and the section.

If one is using an enlarging lantern or a projection lantern, then, in order to get satisfactory lighting, as is well known, the condenser must be close to the negative or slide and must focus the illuminant on the projection lens. The same principle is used for photographing metal sections, and the arrangement of condensers is shown diagrammatically in Fig. 8, which shows the 35 mm. lens A attached to

FIG. 8.

Condenser system for low power photography.

the microscope tube and the section B on the stage (the microscope used is the large "Works" model made by Watsons, London, which has a very wide tube—the inner draw tubes are removed for use with this lens). The condenser D forms a considerably enlarged image of the illuminant C (the 500 C.P. Pointolite Lamp) at E close up to the second condenser F, and the latter in turn focusses the image (after reflection at the 45° cover glass reflector G and the surface of the specimen) on the lens A, as indicated roughly by the dotted lines. The condensers used are $2\frac{1}{8}$ in. diameter, and it is possible to illuminate evenly a section about 1 in. diameter; this is more than required, as the field of the lens is only about $\frac{5}{8}$ in. diameter. Fig. 9 shows the apparatus set up, and Figs. 10 and 11 some of the results obtained.

It is obvious that these low powers are of special value where either the structure is very coarse, or where one wishes to show the variation of structure over a fairly large area. For example, Fig. 10 (× 15 diameters) shows far better than a photograph at, say, 100 diameters, the structure of the sample of overheated steel from which it was taken. Fig. 11 (× 15 diameters) illustrates another type of photograph for which the ordinary microscopic objective would be quite useless; this shows the size and distribution of carbon in an unsound segregated area. This actual example is rather unique, showing, as it does, high and low carbon areas in close proximity.

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With the author's camera and microscope, magnifications ranging from 9 to 23 can be obtained, but with a longer camera it would be quite possible to reach 30 or 40 diameters. As mentioned above, the tube of the author's microscope is very wide and comparatively short (2 in. diameter and $4\frac{3}{8}$ in. long), and this enables one to use practically the full field of the 35 mm. lens; with a narrower tube, of course, part of the field would be cut off. In such cases one may do without the microscope and mount the lens on a small fitting (with either spiral or rackwork focussing) on the front of the camera. In one or two cases the author has done this, and has succeeded in obtaining a $6\frac{1}{2}$ in. circle at 9 diameters (*i.e.*, a field of .72 in.). The definition in this case was not quite perfect round the edge, but it was sufficiently good for the purpose.

It may not be out of place to mention that when taking a photomicrograph without using an eye-piece it is necessary to avoid reflection from any metallic surface inside the microscope tube. The latter should be coated with a dull black varnish, but it is generally advisable to put in a lining of black cloth. Such a lining

FIG. 12.

Illuminating system for lowest powers (up to about ×5).

can be easily made by gumming a piece of black cloth of the required size on to a similar piece of fairly stiff paper, then rolling into a cylinder (cloth inside), which can be slid into the microscope tube.

For still lower powers one may use a photographic lens of 3 in. to 5 in. focus; the one used by the author is a $5\frac{1}{2}$ in. Holostigmat by Watson, and with this he can reproduce from natural size up to about 4 diameters. In this case a different system of illumination is employed. For the 45° reflector a thin lantern slide cover glass is used. (It is possible to obtain thin microscopic cover glasses in sizes up to $4\frac{1}{4}$ in. × $3\frac{1}{4}$ in., but such glasses are very fragile.) A large piece of ground glass is mounted close to the section as shown at A in Fig. 12, and the condenser B throws a parallel or slightly divergent beam of light on this. The idea is to produce an evenly illuminated disc of light on the ground glass, and the light from this is reflected on to the section by the 45° reflector C. Such low magnifications are especially valuable with sections etched with one of the "copper" reagents (such as Stead's, Rosenhain's, or Le Chatelier's), which require a low magnification as a general rule. Fig. 13 is an example of this—it represents a section (×4 diameters) from a small sample ingot (taken for analytical purposes from an

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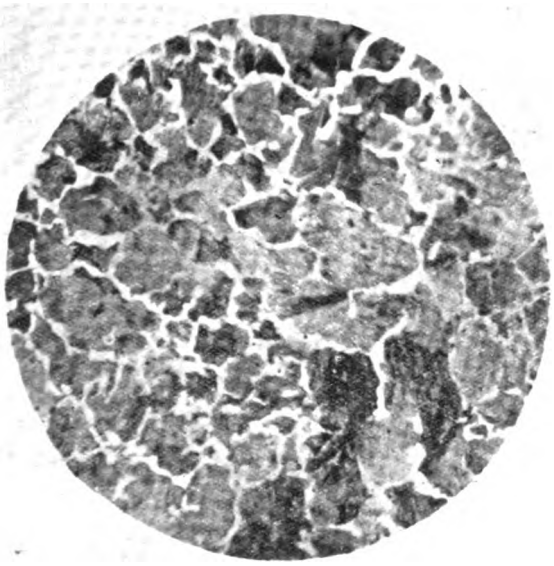

FIG. 4.
Ferrite and Pearlite, using good disc.
× 100.

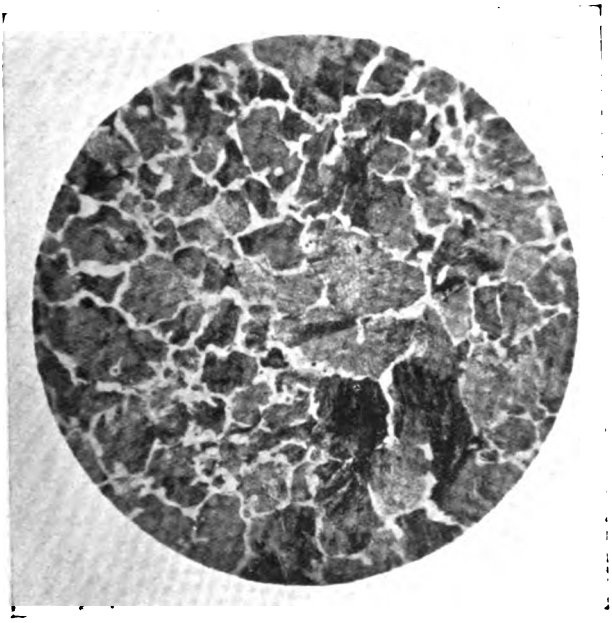

FIG. 5.
Same field as No. 4, but taken with bad disc. × 100.

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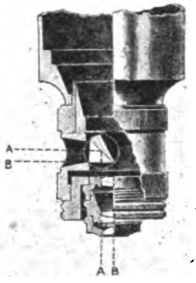

FIG. 6.

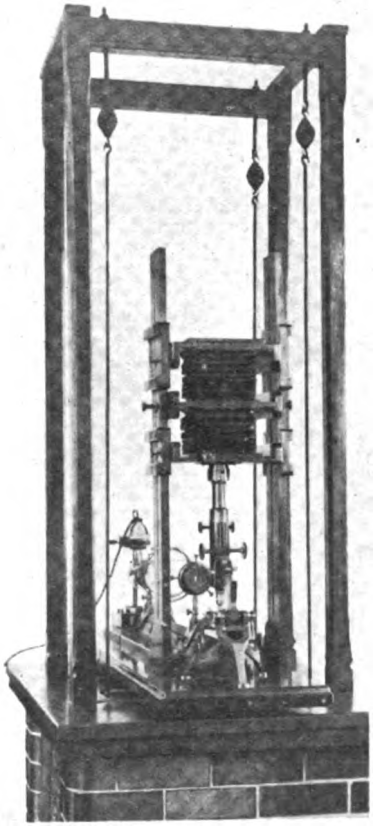

FIG. 7.

Photomicroscope showing spring suspension.

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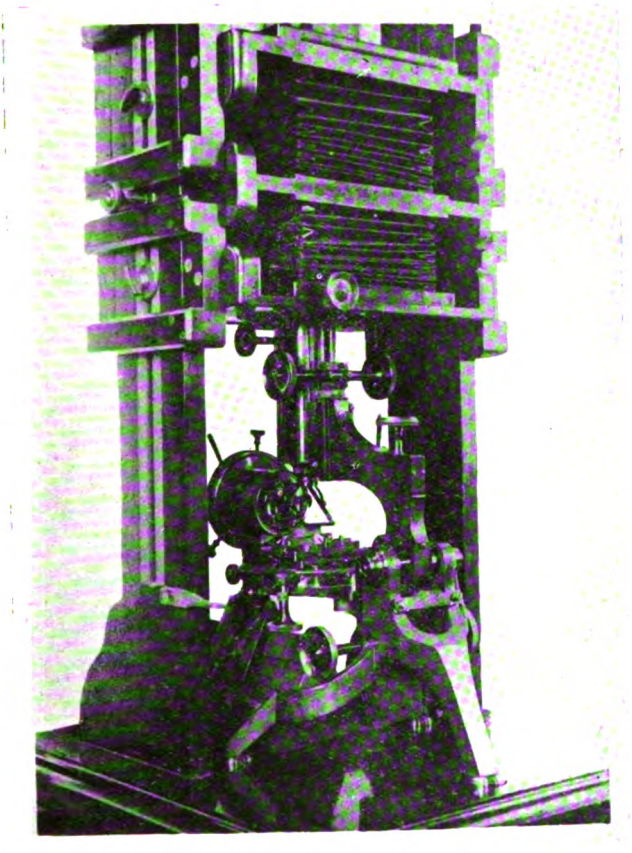

FIG. 9.

Microscope and condenser arranged for low power photography.

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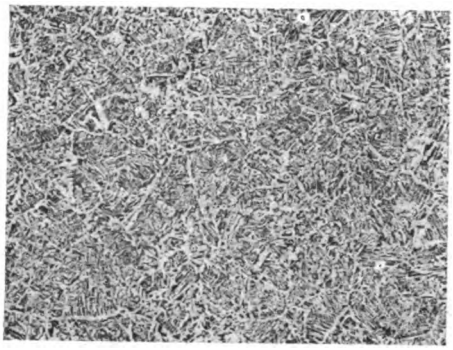

FIG. 10.

Overheated Mild Steel, × 15 diam.

(Reproduced half size—*i.e.*, × 7½ diam.)

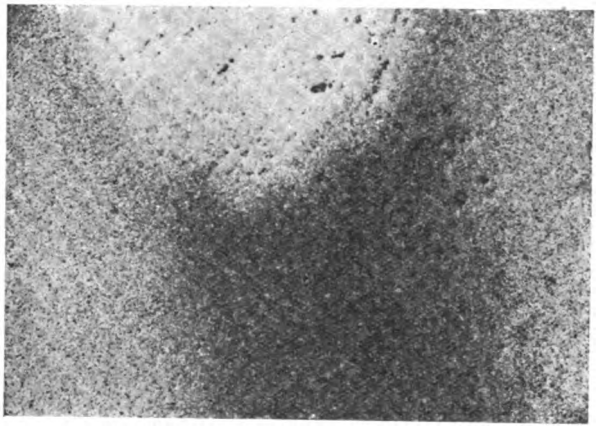

FIG. 11.

Segregated Core in Mild Steel Bar × 15 diam.

(Reproduced half size—*i.e.*, × 7½ diam.)

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FIG. 13.

Chill crystals in small steel ingot (etched cupric reagent), ×4.

FIG. 14.

Section of Burnt File Blank showing decarburisation, × 3.
(Reproduced half size).

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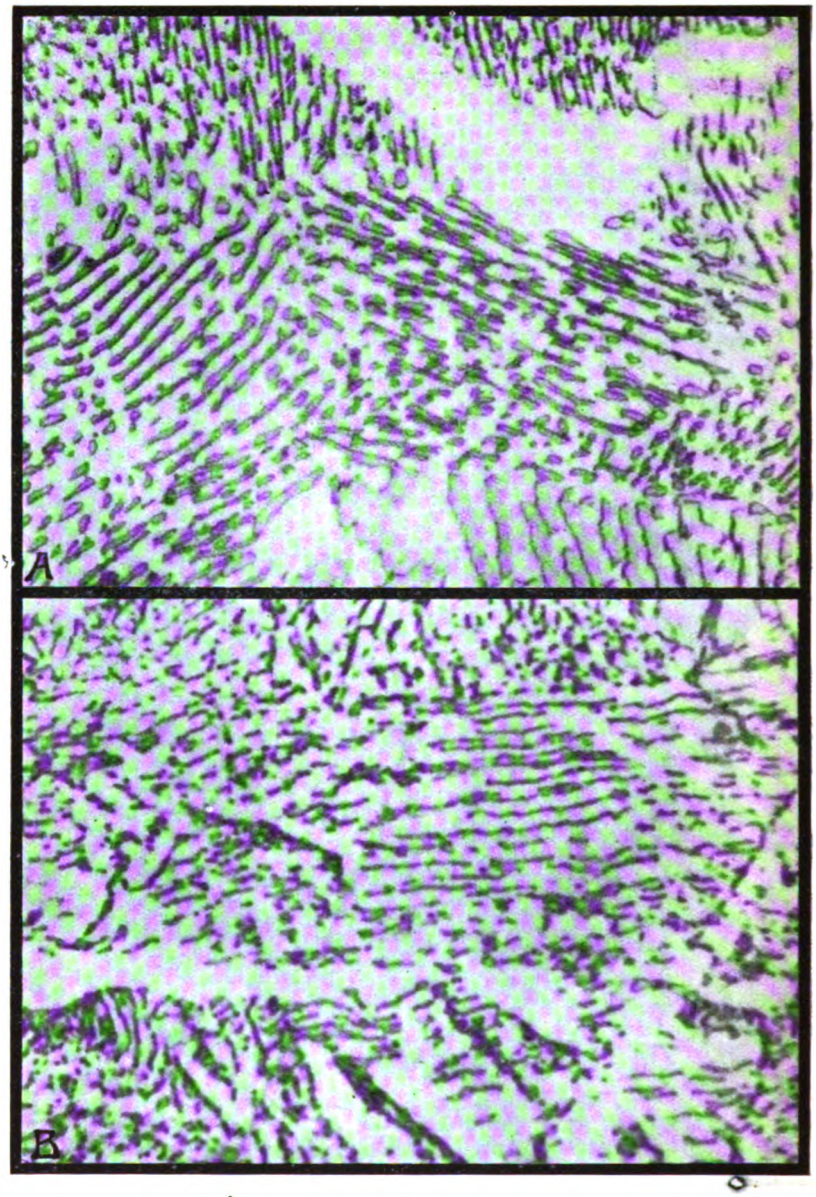

A.—Laminated Pearlite and Ferrite.—× 3,500 reduced to 3,000 Zeiss 2 m/m. apochromat. N.A. 1.4., nonochromatic blue light. (Negative × 1,000 and enlarged.)

B.—Pearlite (finer than A) and Ferrite.—× 3,500 reduced to 3,000. Watson 2 m/m. "Holos" N.A. 1.35, yellow green light. (Negative × 1,400 and enlarged.)

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electric furnace), and shows the development of long chill crystals. Fig. 14 (from a file blank burnt in forging) was also taken by this method, and shows (×3 diameters) the decarburisation formed both in the skin and round the cracks.

A method of illumination similar to the last one was described by F. B. Foley in "Metallurgical and Chemical Engineering" (August 1st, 1919). He used it for low power photomicrographs (at about 7 diameters). For this purpose, however, the author prefers the arrangement shown in Fig. 8, as it gives better detail at these magnifications.

In conclusion, the author wishes to thank the Directors of Messrs. Brown Bayley's Steel Works, Ltd. (and in particular Mr. H. Brearley) for permission to publish the photographs accompanying this paper, and also to Messrs. F. S. and W. H. Nicholds (members of the Laboratory Staff) for their assistance in preparing the photographs and diagrams.

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METALLURGICAL MICROSCOPES AND THEIR DEVELOPMENT.

By LESLIE AITCHISON, D. Met., B.Sc., A.I.C., and F. ATKINSON.

It is assumed that the primary function of this symposium is to bring out the present position in regard to microscopes and also to elicit those improvements which could well be introduced into microscopes with a view to improving the instruments, making them more convenient to employ, and also elaborating the uses to which they can be put. The present notes are written from the point of view of the metallurgist, and primarily from that of the working metallurgist, to whom the microscope is of constant value and usefulness. No attempt is made to discuss the questions from the optician's standpoint, but rather to indicate the needs of the metallurgist in the hopes that the optician and miscroscope manufacturer will be able to meet more and more of these requirements.

In saying anything of modern microscopes it is difficult to avoid constant reference to the products of the Continental makers, and to make comparisons between their microscopes and those produced in this country. This has reached the stage at which comparisons usually take the form of stating how near the British article approaches to the Continental. The position will not be really satisfactory until the reverse of this position is the true one, i.e., until the British article is compared with the Continental on the basis of the superiority of the former and not upon its inferiority.

Speaking as users of microscopes and microscopic outfits, one of the first points that requires attention is the more prompt incorporation in the instrument of those details and fittings which make the use of a microscope less laborious. The Continental makers were always ready to adopt and to incorporate these details, and it would be of great assistance if the British manufacturers would do the same. For instance, the Continental makers would supply a stage micrometer in metal (a great improvement upon those made in glass), marked in tenths and hundredths of a millimetre. The British manufacturer has up to the present given us one marked only in tenths of a millimetre.

A similar matter, and one that causes a good deal of trouble, is the lack, upon photomicrographic outfits, of a really good, reliable and workable fine focussing arrangement which can be operated from the camera end. This objection applies to *all* microphotographic outfits, British and Continental, as none of those made give real satisfaction. For metallurgical work photomicrography is of great importance, and if photographs are to be taken at high powers, *e.g.*, up to 1,000 diameters, the focussing apparatus is of vital importance. Those at present manufactured do not work really well, and cause a great deal of irritation to the operator.

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Connected with the photomicrographic outfit is the trouble which is experienced because of the lack of adequate devices for the prevention of vibration of the apparatus. The greatest proportion of metallurgical photomicrography has to be done in works. Such places are always subject to a fair amount of vibration, which is usually transmitted in a greater or less degree to the apparatus. This almost renders high power photography of the higher order impossible. The problem of vibration is not new, and various efforts have been made to solve it by the makers, but up to the present these efforts have not proved at all successful. The existence of the vibration is one of the factors which limits the development of higher powers in industrial microphotography.

Photomicrography is not possible at all unless the source of light is good and reliable. The arc lamp is not good for photography. It is too uncertain. It is very prone to flicker, and also to give a wandering source. Further than that, it requires a good deal of attention—replacing and adjusting of carbons—whilst it also usually involves the use of a mechanical device for keeping the arc in its correct situation. Lime-light does not suffer from these defects, but it presents the other difficulty, namely, that it is not sufficiently intense to provide a good illumination at high powers, and therefore to allow of short exposures. The specially designed sources of illumination, such as the Pointolite, are distinctly better, and it is considered that this is the form of illumination which will best repay development.

It is obvious, of course, that the improvements indicated above are of little value unless they are accompanied by excellence in the more purely optical parts of the outfit. The critical part of the microscope is undoubtedly the combination of the lenses, and it is probably in this part of the equipment that the standard Continental makes are most missed. There are numerous points about the lenses which could be considered, but one of them can be selected as typical. This is the production of a flat field. In this respect the Continental outfits showed a great superiority, as they permitted photographs to be obtained perfectly sharp at really low magnification (10). This was of immense importance in the study of cast metals and in watching the persistence of the primary crystallisation of a metal through all the subsequent stages of working and treatment. Unfortunately no such good results can be obtained with the usual British lenses.

The usual range of magnification of the modern microscope ends at about 1,500 diameters—particularly in so far as photography is concerned. Unfortunately there are many things which this magnification does not reveal, and which the metallurgist would be glad to investigate. It seems that it might be useful to indicate a few of the points which the invention of a " metallurgical ultra-microscope " might be expected to make plain.

Several such points arise in connection with tempered steel, and although it is not possible to make their significance entirely plain without introducing a good deal of matter apart from microscopical, they may be taken as typical problems. As is well known, hardened steel consists essentially of a solid solution of iron carbide in iron. If this solution be tempered, a certain change takes place in it, which is reflected in the mechanical properties of the steel, which becomes softer and tougher. This change is usually (and probably quite correctly)

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ascribed to the splitting up of the solid solution, the iron carbide being precipitated in a fine state of division throughout the solvent iron. That this explanation is correct in its outline is more than probable, and when the tempering has proceeded to something like completion the presence of the carbide is easily detected. The early stages of the decomposition are practically incapable of observation with the present microscopic means which are available, but this is the portion of the process which is of the greatest interest and importance. It is almost impossible at the present time to say at what temperature the decomposition of the solid solution commences or how it proceeds. In many carbon steels the maximum stress, which in the ordinary way is supposed to decrease when the tempering temperature increases, actually increases at tempering temperatures near to 400° C. Typical results are:—

TABLE 1.

Steel	Heat Treatment	Max. Stress tons/sq. inch.
0.3% carbon	Quenched 850°C. ... temp. 15°C.	50.5
	,, ,, ... ,, 100°C.	49.6
	,, ,, ... ,, 200°C.	49.4
	,, ,, ... ,, 300°C.	47.1
	,, ,, ... ,, 400°C.	50.1
	,, ,, ... ,, 500°C.	46.8

It is quite likely that if the constitutional changes going on within the steel could be examined microscopically, and a better idea of these changes formulated, the explanation of the peculiar happenings would be found. This would require a very high power—something probably of the order of ten times as great as the present powers.

Similiar problems arise in connection with the tempering of the alloy steels. In the nickel chromium steels, for instance, a property known as temper brittleness is shown by steels which cool slowly from or through a certain range of temperature, *e.g.*, 425° C. to 550° C. In all other respects the mechanical properties of the steels are the same whether cooled quickly or slowly. The effect of different methods of cooling from this temperature upon the toughness is shown in Table 2.

It is inconceivable that there is no difference at all in the constitution of the two steels, but the present microscopic methods fail entirely to detect the difference (see Figs. 1 and 2). It is possible that higher powers would make the detection possible. The same powers might also give an explanation of the peculiar impact values which are obtained from the alloy steels by tempering at comparatively low temperature, *e.g.*, 150° to 350° C. The accompanying curve (Fig. 3) shows the values which are customarily obtained, and in addition shows

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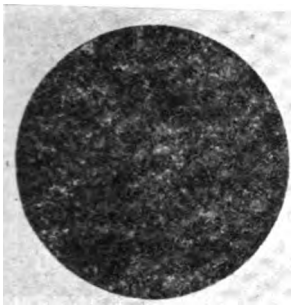

FIG. 1.

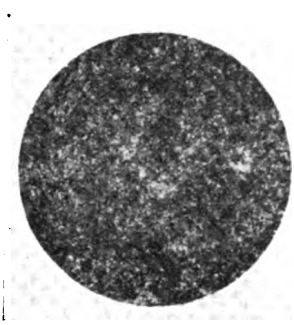

FIG. 2.

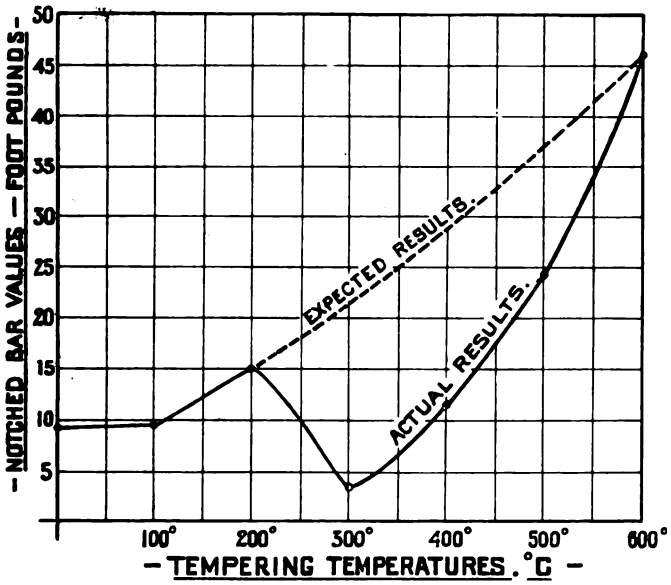

FIG. 3.

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the form of the curve which might reasonably be expected. Here again there is surely some constitutional alteration taking place, and it might reasonably be hoped that a sufficiently high powered Microscope would reveal it.

The theory which has probably had as much effect as any other upon recent scientific metallurgy is that known as the " amorphous cement " theory. This theory postulates the existence, between the crystals of a metal, of a thin layer of amorphous material which both

TABLE 2.

Tempering Temperature.	Notched bar value on tempered specimens.	
	Cooled in air after tempering.	Cooled in water after tempering.
400°C.	8	8
500°C.	18	18
550°C.	7	30
600°C.	8	41
650°C.	8	53

separates and binds together the individual crystals. The properties of this amorphous metal are necessarily different from those of the crystals which it surrounds. The evidence for the existence of this layer is largely circumstantial, and though the evidence is powerful it would be decidedly stronger if the cement could actually be revealed. If a power of 10,000 failed to produce any further evidence of its existence it would seem difficult to imagine that it is really there.

Duralumin is a metal which has distinctly peculiar properties. If duralumin be quenched in water from a suitable temperature it is soft at first, but after standing for a time, e.g., 24 hours, the metal becomes quite hard. This change of properties is bound to be accompanied by some change of constitution, and a possible explanation of this change has recently been put forward by Dr. Jeffries. It seems certain, however, that the application of higher powers of microscopic examination would help materially in the investigation of this problem.

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PHOTOMICROGRAPHS OF STEEL AND IRON SECTIONS AT HIGH MAGNIFICATION.

By Sir Robert Hadfield, Bart., D.Sc., D.Met., F.R.S., and Mr. T. G. Elliot, F.I.C.

Owing to the importance of the study of Microstructure much attention has been given to this subject since the days when the late Dr. H. C. Sorby, F.R.S., of Sheffield, originated, in 1857, this method of examining structures of various materials, including Iron and Steel. Indeed, one of the most striking features of the progress of Metallurgy in recent years is the great development of the use of microscopical methods of investigation. We submit some photomicros, Figs. 1 and 2, Plate A, representing some of the early work of Dr. Sorby at 9 magnifications. We also submit as a comparison, and in order to demonstrate the great advance in Metallography, Photomicrographs Figs. 3 to 25 showing later work of the writers of this Paper, in which magnifications are dealt with of 100 and up to no less than 8,000.

In carrying out this work, our best thanks are due to Mr. H. Wrighton, B.Met. for the assistance he has rendered and for the care and skill he has exercised in preparing the Photomicrographs accompanying our Paper.

One of us well remembers his conversations with Dr. Sorby regarding the micro study of his own early specimens of Manganese Steel, in 1883-1887. Dr. Sorby never turned away the youngest enquirer, and he little imagined when first describing his method in 1857 what an important aid this would eventually prove to Metallurgy. This is another instance of the great value to the Metallurgist of original work by the pure Scientist. Next to Sorby, this important branch of investigation owes more for its development to Arnold and Osmond than any others. It has been further advanced by Sauveur, Stead, Le Chatelier, Carpenter, Howe, Martens, Robin, Rosenhain, and many others.

Sorby bequeathed £15,000 to the Royal Society for the establishment of a Fellowship for the carrying on of original Scientific Research, the object specified being "to promote the discovery of new facts rather than the teaching of what is known," and stated that as far as possible the Researches should be carried out at the University of his own native City, Sheffield. To this Englishman, Sorby, the whole world has fully and freely given the credit of originating this important form of research which enables the structure of Iron and

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its Alloys, including in that term the material generically known as "Steel," to be examined and understood in a manner which was before not possible. "Steel" is a wide term and to-day covers material which is practically pure Iron, for example, products containing 99.9 per cent. of Iron which offer high resistance to corrosion and oxidation and containing practically no Carbon, up to the material used for wortle or drawing plates which contain even more than 2 per cent. of Carbon.

Twenty-five years ago there were scarcely half-a-dozen Steel Works in the country which could lay claim to the possession of a Microscope suitable for metallographical examination. At the present time it may be safely said that no steel works of any size is without one. Nor is the use of the Microscope confined to the examination of Iron and Steel sections, for those engaged in the investigation of non-ferrous metals and alloys find its aid equally useful.

The history of Metallography, short as it is, is beyond the scope of the present paper. Naturally such history to be complete would record the improvements which have taken place in the construction of Lenses for metallographic work. One of the most important of these was the introduction of the Apochromatic Objective by means of which increased resolution was obtained, an absolute necessity for successful high power photomicrography. Unfortunately, as this Country had occasion to find out on the outbreak of War, the making of these objectives has in the past been largely in foreign hands. Steps are being taken to remedy this, and there is every reason to hope that here, as in other directions, in future, we shall be rendered entirely independent of the foreigner.

Great as have been the advances made in the microscopical examination of Iron and Steel, there still remains a wide field for exploration; for example, as regards methods which will enable increased magnifications to be obtained. It is wonderful what can be accomplished by the aid of the human eye alone, and even to-day the finest quality of crucible cast steel is, in its ingot form, first packed or sorted over in this manner. It is stated that an experienced workman can, by the eye, detect from the appearance of the fracture differences as small as .05 per cent. to .10 per cent. of Carbon. No doubt for many purposes an ordinary strong magnifying glass will tell much and more than the unaided eye can do, but when it is desired to reveal structures minutely, then the microscope is called in with great advantage. Magnifications of 10 or less, upwards to 1,000 or 1,500 are those most commonly used in metallography. Photomicrographs of larger magnifications than 1,500 have been rarely published. The Authors have, however, carried out experiments in order to obtain photographs of 5,000 and even 8,000 magnification, which may be of interest to this Society.

The very fine structures met with in alloy steels have made it desirable and induced the Authors to prepare in their research photomicrographs at higher magnifications than have hitherto been obtained. With great care and attention to necessary details, particulars of which are described in this Paper, we have been able to

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obtain photographs of Iron and Steel sections at the high magnification of 8,000 diameters. To give an idea of what this means, it may be mentioned that the diameter of the actual field shown in a $3\frac{1}{4}$" circle photograph at this magnification is only .00041" or 1/2460". The actual area of this field examined is .00000013 square inches. The polished section under micro-examination is usually about $\frac{1}{4}$ in. square. If the whole of this area were magnified 8,000 times it would yield a square about 55 yards by 55 yards, occupying an area of approximately 3,000 square yards, that is to say, not far away from three-quarters of an acre.

As is well known, the modern Microscope consists of two systems of lenses, the objective and the eye-piece. The objective gives an enlarged image of the object, and the eye-piece further magnifies this image. The high power photomicrographs given in this Paper are simply high magnifications by means of the eye-piece and extra camera extension of the image given by a 2 mm. objective, or in the case of the 8,000 magnifications by a 1.5 mm. objective. Whatever may be the quality of the image given by the objective—for example, as regards resolution—that quality is reproduced in the magnified image of the eye-piece. Thus, if the objective gives a blurred image, the blur is simply magnified. In other words, it is just as though a lantern slide were projected on the screen; if the slide is a good one we get a good picture, but if bad the picture will be no better because it is magnified. The essential aim, therefore, is to get a very clearly resolved image. This needs a special quality or virtue in the objective, and this virtue is called its resolving power.

For photomicrography at high magnifications, it is specially essential that an objective of high resolving power should be used. The effect of magnification without resolution is well illustrated by Figs. 3, 4 and 5 on Plate B. These photographs are all at 600 magnifications, but taken by objectives of low, medium, and high power respectively. In No. 3 the dark ground mass is left unresolved. No. 4 shows some resolution of this dark ground mass, but in No. 5 it is practically completely resolved into its two constituents, Ferrite and Cementite in lamellar form. In the course of a search for a really good 2 mm. oil immersion objective, for photomicrographic research, we found that results obtainable with a moderate Achromat, compared with those obtained with a good Apochromat, showed differences at least as great as is illustrated in Figs. 4 and 5.

An illustration of the microstructure of an Annealed Alloy steel, containing .84 per cent. Carbon and 1.12 per cent. Chromium, is shown at four different magnifications in Figs. 6, 7, 8, and 9 on Plate C. Although the resolution of the structure is the same in Figs. 7 and 8, because the same objective was used in each case, the effect of the increased magnification is to show in a striking manner the alternate white and dark constituents of the lamellar pearlite. This effect is further emphasised in a photograph of the same section at 8,000 magnifications, shown in Fig. 9. There is no doubt that this magnification taxed the lens somewhat beyond its capacity; however, the photograph is certainly a good one and worth including, if only to show the limit obtainable with the apparatus available at the present time.

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Photomicrographs of Diatoms at 5,000 magnifications and over, taken by transmitted light, have been published; but so far as we are aware steel sections at such a high magnification have not been available. This may be easily accounted for by the difficulties in the way. Although, unfortunately, we are unable to indicate an easy path by which these difficulties may be avoided, we propose to show the means by which we endeavour to overcome them.

We have already laid stress on the need for an objective of high resolving power capable of giving good definition when combined with a properly compensated eyepiece of high magnifying power.

Probably the next most essential point is that the specimen to be photographed be properly etched. Deep etching is fatal; it causes pits and furrows in the surface of the piece which extend beyond the range of depth of focus, which with a high power objective, is naturally very limited. Therefore the most delicate etching is necessary, and this we find is usually best obtained with 5 per cent. Picric Acid in Alcohol.

The illumination of the specimen for photography is the next subject for attention. For high power photography the lighting should be as intense as possible. We use a 20 ampere arc lamp of the hand fed type, and this is found preferable to one mechanically fed. It is simple, has no mechanism to get out of order, and the carbons are not liable to re-adjustment at the critical moment, just when the plate is being exposed. Moreover, mechanically fed carbons are never so firm and free from vibration as those of the hand fed types. Alternating current at about 70 volts can be used with perfect success on a 20 ampere hand fed lamp, if cored carbons are used. This is a point on which emphasis should be laid, for the makers of our apparatus have always laid stress on the necessity for direct current for photomicrographic work. Tungsten Arc and Mercury Vapour Lamps have been more recently introduced for photomicrographic work, but we have had no opportunity of testing them.

The vertical illuminator attached to the Microscope should be a plain glass disc. We find a prism unsatisfactory for this work. The light should be focussed on the diaphragm of the vertical illuminator, and of course it must be perfectly central with the Microscope and the camera.

The iris diaphragm of the illuminator should only be closed as much as is necessary to get sufficient of the field sharp. Further closing of the diaphragm not only interferes with the resolution, but produces false images. An example of this effect is shown in Figs. 10 and 11, Plate D. Fig. 10 illustrates the result produced by closing the diaphragm too much, and Fig. 11 shows a correct image obtained by proper adjustment.

The diaphragm in the condenser system should be closed so that only the area to be photographed is illuminated.

For apochromatic objectives, a blue screen as a light filter should be used, and ordinary photographic plates. The specimen is focussed first of all on the ground glass screen of the camera, and finally adjusted

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with the clear glass screen and the aid of the focussing magnifier. There is one point that has not been mentioned, which is quite obvious, and that is the necessity that the mounting of the whole photomicrographic apparatus should be perfectly rigid and free from vibration.

We have selected a few photomicrographs in order to show the effect of increasing magnifications on the same section, and also to illustrate well-known types of microstructure at high magnifications. The objectives used in obtaining photographs at 1,500 and over are stated on the plates.

The photographs on plates A, B, C and D have already been dealt with in the text.

PLATE E. — Figs. 12, 13, 14 and 15, show the microstructure of a Nickel Chromium Alloy Steel in two different conditions. Even at 1,500 magnifications the structure is seen to be very fine and close textured ; it is rather more clearly defined at 5,000 magnifications, but a structure of this kind is very difficult to photograph owing to the want of contrast obtained even with the most careful etching.

PLATE F. — Figs. 16, 17, 18 and 19 show the structure of Grey Cast Iron. The black constituent is Graphite, and the ground mass Pearlite. The four photographs on this plate illustrate very strikingly the advantage of higher magnifications in order to see clearly the details of a fine Pearlitic structure.

An additional photograph (Fig. 19a) is given on Plate F, which has been obtained by making an enlargement of the negative from which Fig. 18 was obtained. The enlargement has been so adjusted that its magnification is 5,000 ; a comparison is therefore obtainable with that of Fig. 19, which has been obtained by the direct method. There does not appear to be much to choose between the two Photographs in this instance, but in the case of more complicated subjects such as those illustrated in Figs. 20 to 22 on Plate G, the direct method of photomicrography, although very much more difficult than the indirect one of enlargement, is far preferable to the latter because the choice of field to be photographed is made at high magnification—an important advantage.

PLATE G. — Figs. 20, 21 and 22. Photographs 20 and 21 show the microstructure of a Carbon-Chromium steel in two different conditions, magnified 8,000 diameters. The former is a Sorbitic Pearlite structure, and the latter consists of Martensite and Troostite (black areas). — Fig. 22 shows the microstructure of a quenched Carbon steel at 8,000 magnifications, and is Troosto-Martensite.

PLATE H. — Figs. 23, 24 and 25. These photographs show the microstructure at 5,000 magnifications of a steel containing 1.41 per cent. Carbon in three different conditions. Fig. 23 is a typical Pearlite and Cementite structure ; Fig. 24 a Martensitic structure, and Fig. 25 a structure of mixed Troostite and Cementite.

The value of higher magnification especially as illustrated in Figs. 8, 9 and 19 can be emphasised as a result of this research. These Photographs at higher magnifications show in a striking manner the details of a structure which at lower magnifications are only

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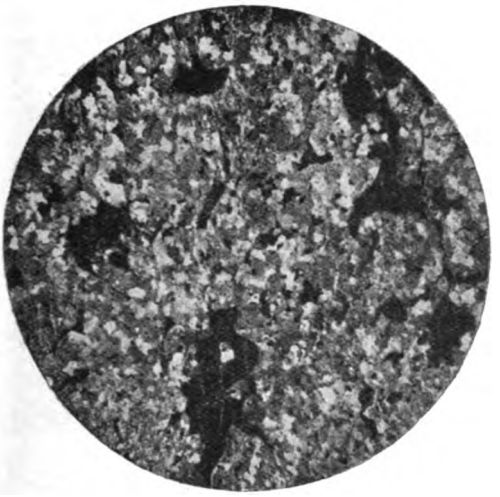
PLATE A.

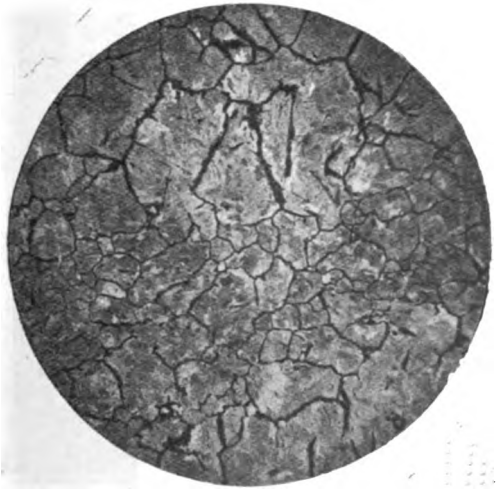
Examples of early Photomicrographs from Sorby's Paper to the Iron and Steel Institute, 1887, "On the Microscopical Structure of Iron and Steel."

FIGURE 1.



Photomicrograph by Sorby.
Magnification 9.
Hammered Bloom Carbon .05%

FIGURE 2.



Photomicrograph by Sorby
Magnification 9.
Blister Steel, Longitudinal Section.

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PLATE B.

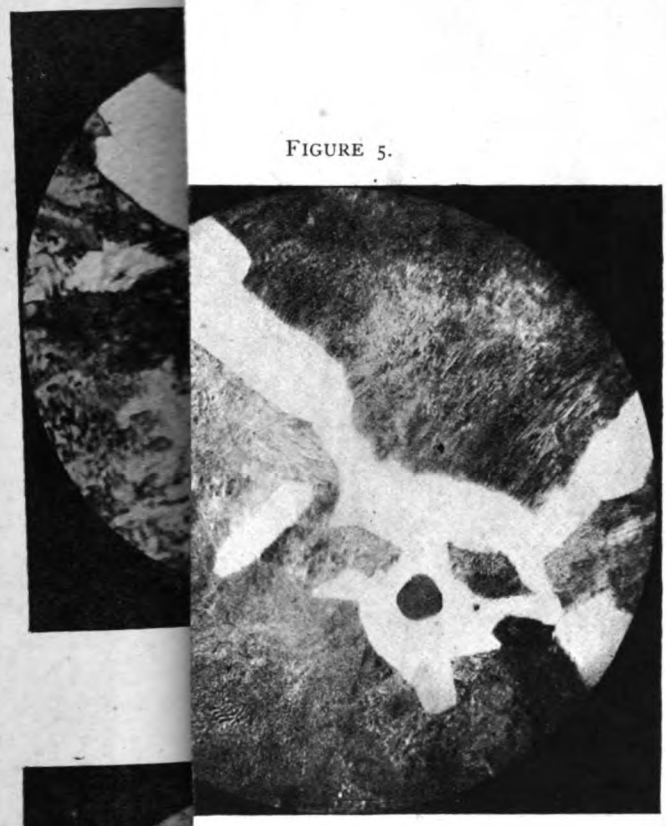

FIGURE 5.

Magnification 600.

2 MM. APOCHROMAT.

ent had the following composition:

	P.	Mn.
9	.034	1.00%

n.

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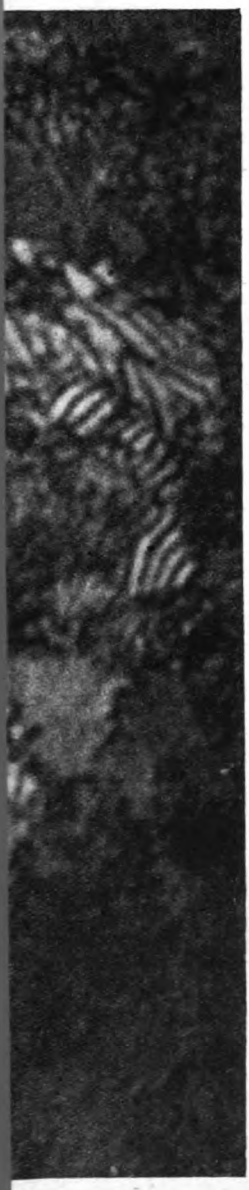

ARLITE.

45 1.12 .12%
n. Cr Ni.

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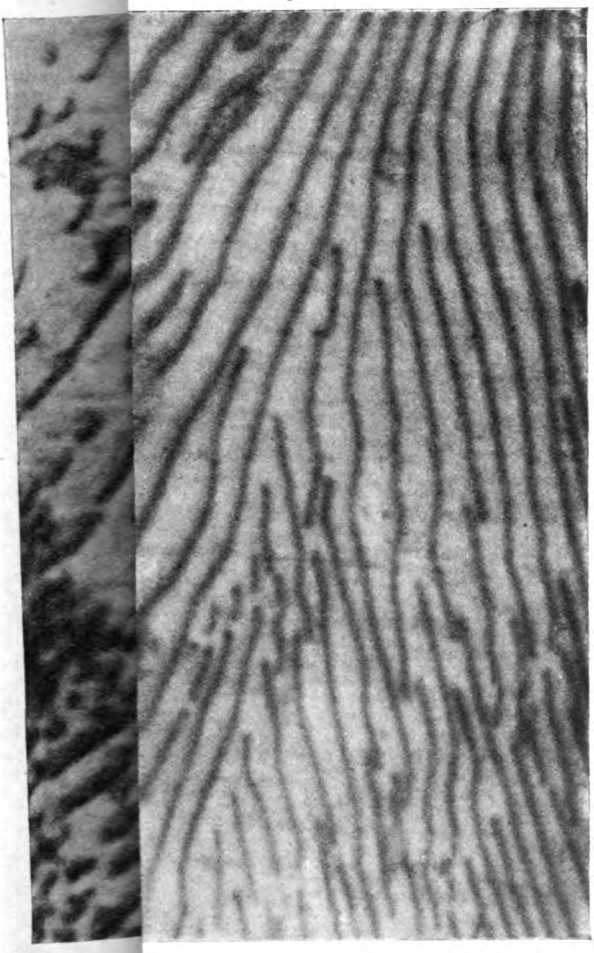
PLATE D.

FIGURE 11.



agnification 5,000.

is Diaphragm.

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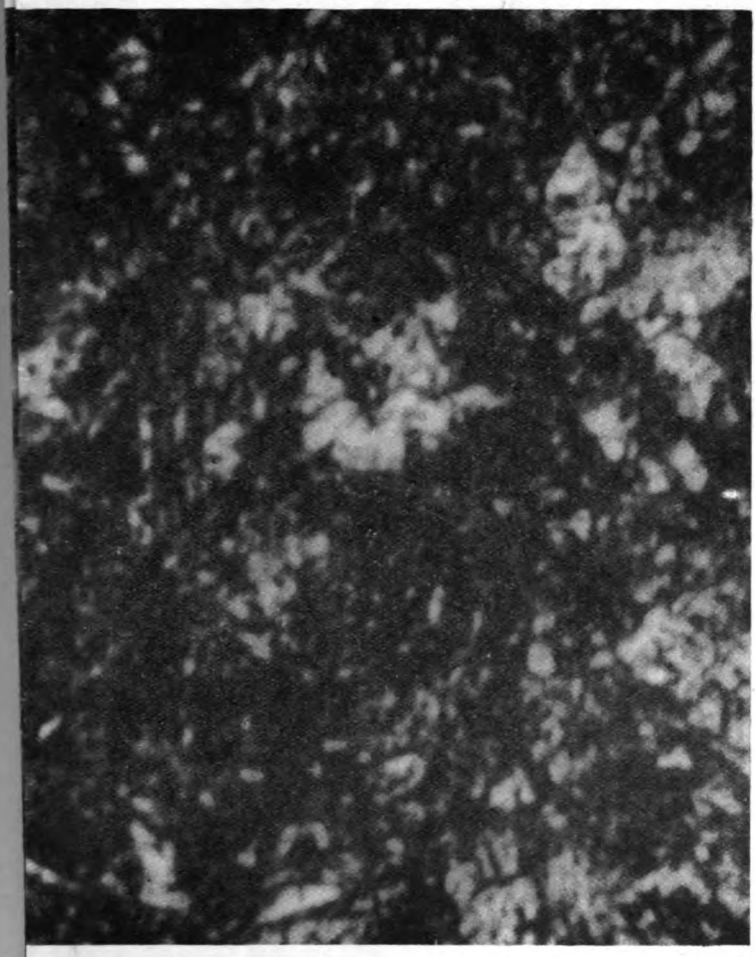
FIGURE 15.



Magnification 5,000.

Quenched and Tempered.

ORBITE.

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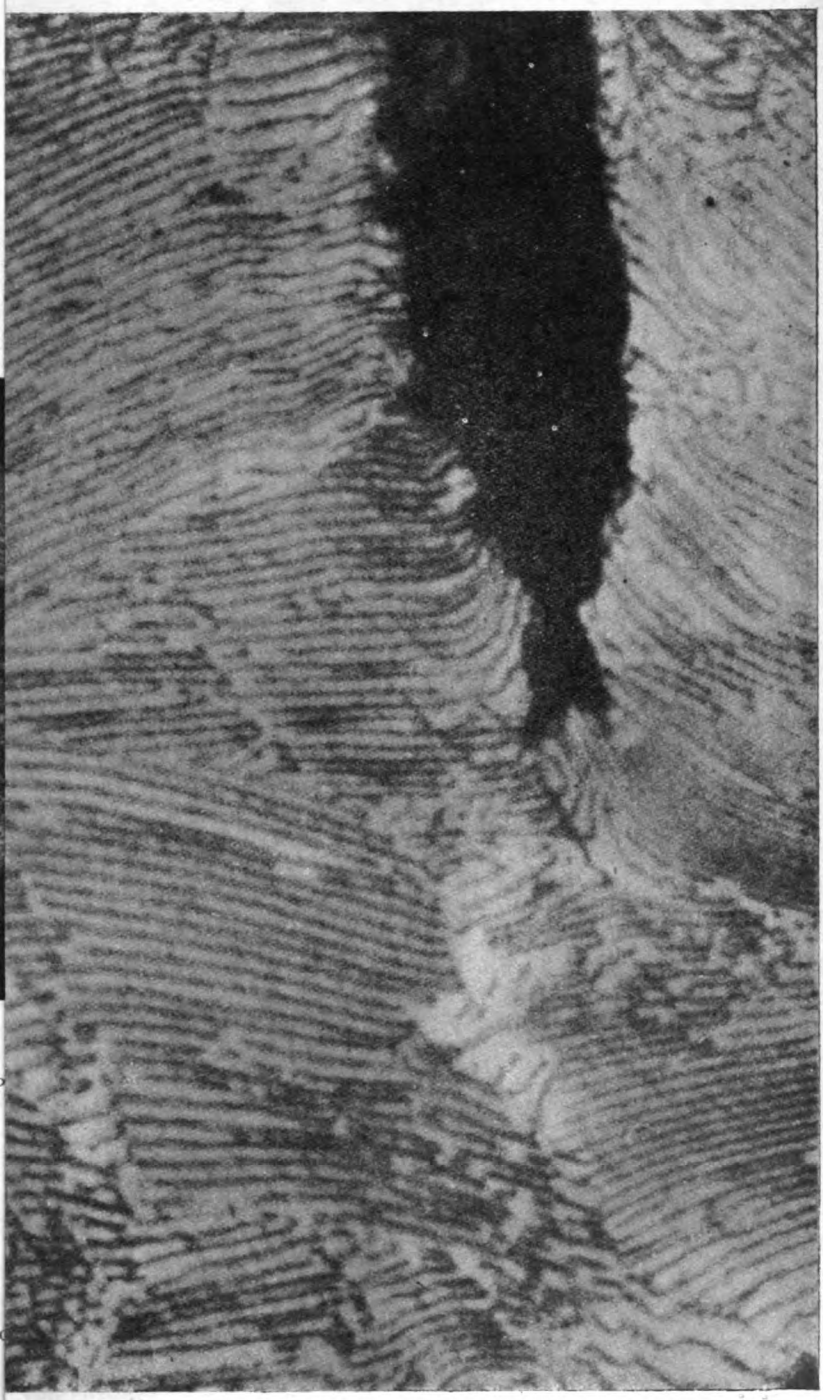
FIGURE 19a.



Magnification 5,000 approx.
RGEMENT FROM NEGATIVE OF PHOTOGRAPH 18

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T.
E.

Cr.
2.51%

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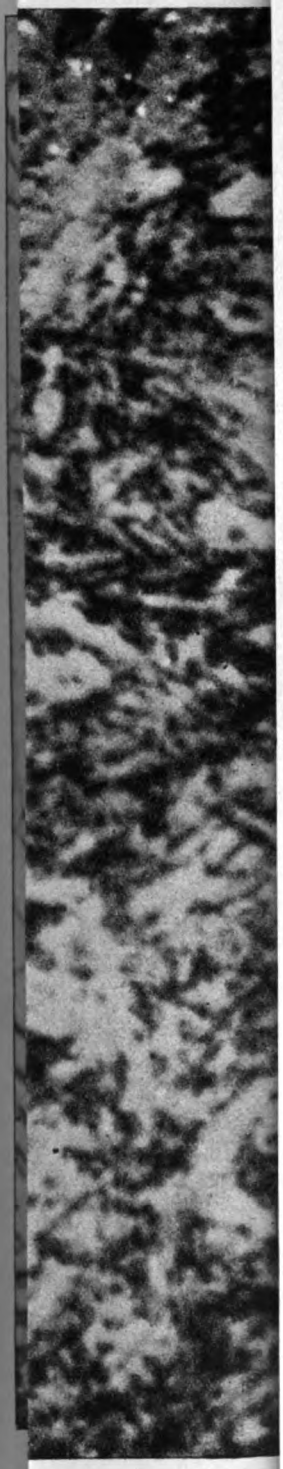

ing composition;

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very indistinctly seen; at the same time we are quite alive to the fact that they have not led us to any absolutely new discovery in the microstructure of Steel, and it is quite evident that there is an important field open for further investigations in this direction.

During the last few months we have been prosecuting enquiries in different directions with a view to obtaining apparatus which would enable us to attain much higher resolution than has been practicable with that at our disposal. While so far we have not been able to do this, several makers of apparatus and objectives in this Country are working at the problem, which we feel sure will soon be solved.

We have also been specially interested in the possibilities that might lie in the use of Ultra-violet Light for Photomicrography applied to Metal Sections. Who knows what new order of Phenomena may not be brought within our vision by the use of such apparatus. Researches are being made in this new field, and we all hope that such labours will be crowned with success.

In conclusion it is hoped that by presenting these Photomicrographs interest will be aroused in this special subject and that others will press forward investigations from which our general knowledge of the subject will benefit; also that the makers of the necessary Apparatus, whether Microscopes, Lenses or Lighting Appliances, will come forward with new developments which will enable still further fields to be explored in the now Unknown.

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THE HIGH-POWER PHOTOMICROGRAPHY OF METALS.

By F. C. Thompson, D.Met., B.Sc. (Lecturer on Metallurgy in the University of Sheffield).

I.—General.

The high-power microscopical examination of metals is a matter of the greatest importance.

As Prof. Abbe has pointed out, however, and this forms practically the whole of the sermon which the author desires to preach, " empty magnification " unaccompanied by a corresponding resolving power is of no service whatever to the metallographer.

As is well known, it is impossible to produce a microscopical rendering of a point other than as a disc of definite dimensions the size of which depends on (1) the numerical aperture of the objective, (2) on the wave-length of the light employed, and (3) on the magnification. The diameter of this spurious disc $D = \frac{m \times \lambda}{2 \text{ N.A.}}$ where m is the magnification, λ the wave-length of the light used, and N.A. the numerical aperture of the objective. It will be at once seen that the image becomes less and less sharp as the wave-length of the light increases and as the ratio of the total magnification to that produced by the objective itself is raised.

As shown in Fig. 1, a succession of points may thus, if sufficiently near each other, merge into an apparently continuous line, the true structure of which would never be realised. Sorbite might in this way simulate pearlite. A very beautiful illustration of this effect in a diatom is given by Spitta, " Microscopy," Fig. 3A, Plate I. It will further be evident that a sorbite in which the diameter of the spurious disc exceeds the distance between the carbide globules will appear practically structureless, Fig. 2A, and that pearlite, the distance between the laminæ of which does not exceed this diameter, will lose its structure, Fig. 2B. The matter, therefore, is of very real practical import.

Abbe has shown that in the absence of certain diffraction spectra a line may be duplicated, or even rendered as three. Although in metallurgical work such results are unlikely—they would, for instance, double or treble the fineness of a laminated eutectic—the possibility of such spurious effects at very high magnifications should always be borne in mind.

According to Spitta the limit of magnification to which it is permissible to go with light of wave-length 540 $\mu\mu$ must never exceed 1,000 times the numerical aperture of the objective.

It would thus appear that the best method of approach to the very high magnifications suggested lies at the present time in the use of ultra-violet " light " of very short wave-length. Since glass is opaque to such vibrations, quartz or fused silica must be used as the optical material of all lenses, vertical illuminators, etc. In connection with metallographic work, since the objective acts as its own condenser, and since no slips or cover glasses are required, such a system is much cheaper than it can be when using transmitted

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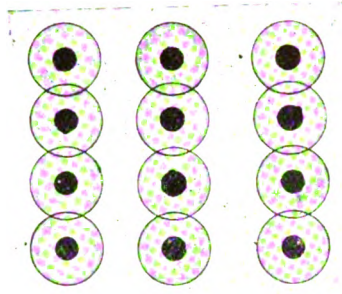
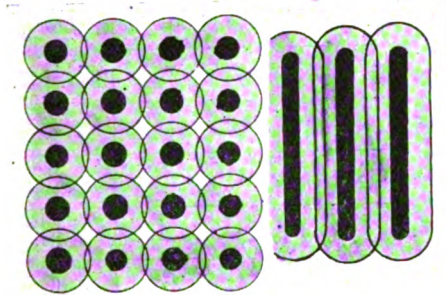


FIG. 1.

Effect of Halo in Producing a Spurious Lamination.



A B

FIG. 2.

Structureless Rendering of Sorbite or Pearlite.

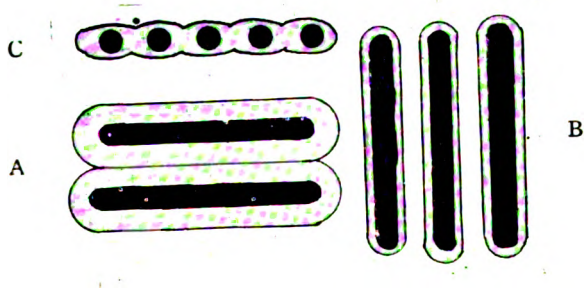


FIG. 3.

Effect of Prism Illuminator.

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"light." The lenses in the objective are constructed of fused silica, those of the eye-piece of quartz. A mixture of glycerine and water of the required refractive index is used as an immersion liquid, and focussing is carried out by the use of a fluorescent screen. So far as the author is aware the highest power silica objective so far made is the 1.7 mm. with 1.25 N.A. In virtue, however, of the shortness of the wave-length used, 275 $\mu\mu$, this is equivalent to about 2.5 N.A., using white light, and according to the rule given above could be used for critical work up to 2,500 diams., which would be obtained with, say, a × 15 eye-piece and a camera length of 31 c.m.s. There appears to be a very big field of usefulness for this system in metallographic research work.

II.—The Davidson "Super-Microscope."

The claims made for this instrument in connection with very high magnifications—up to 15,000 diams.—render a consideration of its capabilities germane to this paper. In essence, an image is formed in the usual manner by a microscope objective, which image is then magnified by a second microscope, with or without an eye-piece. Such a procedure demands for the highest magnifications an amplification of the primary image so high that no objective at present made will stand it. In theory the instrument is unsound, and in practice, so far as the author's observations go, the results at high magnifications are very poor. Through the kindness of Sir Robert Hadfield the apparatus was sent to the author some two or three years ago for investigation. Since then the mechanical side has been considerably improved, the optical arrangement remaining, however, unchanged. Quite recently another opportunity has arisen for his observation of the instrument, but his view is unchanged. In the trial two test objects were chosen, one a very fine sorbitic structure in a quenched and tempered tool steel, the other a normalised Bessemer steel with 0.4 per cent. carbon, and 1 per cent. manganese, the pearlite in which was finely laminated. With a magnification of 1,000 diams., using Zeiss lenses and the ordinary apparatus, both objects were easily resolved. At the same magnification, however, the "Super-microscope" failed entirely. The sorbitic material appeared structureless, while in the case of the pearlite only the faintest suggestion of lamination could be detected. At higher magnifications the apparatus is utterly valueless.

The very claim put forward for the instrument that it possesses great depth of focus is in itself an admission that the resolving power is poor, since these two factors vary inversely as each other. Since for the purpose at present under consideration, viz., high magnification of metallic structure, depth of focus is of no importance, while resolution is a matter of prime weight, the remarks previously made are still further substantiated.

For other purposes, as a telescope, or for low power examination of a metallic fracture where great depth of focus is quite necessary, the apparatus probably offers very real advantages. In particular, perhaps, may be mentioned direct measurements from some distance of changes in length, such as are needed in a determination of co-efficient of thermal expansion.

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III.—The Reichert Microscope.

This instrument, which is too well known to need description here, has often been regarded as a convenient apparatus for use in those industrial establishments where convenience and rapidity of working are, perhaps, of somewhat greater importance than the very finest definition and resolving power. An investigation recently made by Professor Carl Benedicks and E. Waldow (Jern-Kontorets Annaler, 1918, 537) has shown, however, that far from such being the case, photographs of the very highest quality can be obtained. Several micrographs published by these workers at 1,200 diams. leave little or nothing to be desired. The perfection is further illustrated by an enlargement at 3,500 diams. which constitutes one of the most excellent photomicrographs of steel at such a magnification ever obtained. This magnification, however, has only been used to show what sort of effect is the best at present obtainable, and does not represent one which will yield critical results. Around the globules and laminae of Fe_3C are thick black halos up to and exceeding 0.5 mm. thick.

The authors point out the much lower quality of picture obtained when the prism vertical illuminator is used as compared with that when the plain disc is chosen. This fact, first pointed out by Professor Benedicks himself, is one of prime importance in connection with high power microscopy. Since in one direction the prism cuts off half of the back lens of the objective, the resolving power is curtailed accordingly. To pay big prices for Zeiss lenses of high N.A. and then deliberately to cut down by the prism illuminator the resolving power to much less than that obtainable with a lens of similar focal length at a fraction of the cost, argues a very poor acquaintance with the theory of the instrument. Since this loss of resolution operates chiefly in one direction, there is a tendency for a circular object to be drawn out into an ellipse. Further, rows of globules oriented in the direction of the longer axis of the ellipse are much more likely than ever to be rendered as a continuous band, while laminated structures may appear structureless or be correctly resolved, according to the direction, Fig. 3. The marked superiority of the disc should need no further emphasis.

As one would expect, the strength of the source of light is shown to be without effect on the quality of the photograph produced. When vibration is considered, however, and this is rarely absent from steel works laboratories, the much shorter exposure required with powerful arc illumination, renders it then possible to obtain sharper negatives than with weaker lighting. In connection with vibration it is suggested that the objective should be separated from the body tube, which will result in a considerable decrease of mass in those parts specially sensitive to vibration, whereby the amplitude of the latter will be reduced and non-recurring.

While considering this point, the following is of importance. Given a certain primary image, this can be magnified in two ways. In the first place, it may be eye-pieced strongly, or alternatively, an eye-piece of lower magnification can be used with a long camera extension. Given absolutely rigid conditions there does not appear to be very much to choose between the two methods, although perhaps the long camera

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is better since, in general, a larger field would be obtained. In cases where vibration may make its influence felt, long camera lengths rarely yield satisfactory results, since the extent of the oscillations increases with the length. It would appear, therefore, that in this case on the few occasions when it is necessary to push the magnification of a given image as far as possible, it is advisable to use a high eye-piece and short camera extension rather than the reverse.

In connection with the use of the projection eye-pieces it was discovered that the setting, *i.e.*, the relative positions of eye and field lens, which requires adjustment for different lengths of camera, is dependent not only on this and on the ocular used, but also upon the objective. The effect of the latter is shown to be considerable, and the statement made that "the possibility of movement of a projection eye-piece is practically superfluous," must be admitted to carry weight, although it is at variance with present notions. Four diagrams are given in which the camera length is related to the best setting of the eye-piece for objectives of different focal lengths.

In conclusion, another direction in which modifications of existing methods might be of value may be pointed out. Cases may well arise in which extremely oblique rays would reveal a structure in what, when viewed directly, appears to be a structureless constituent. The insertion of suitable diaphragms behind the back lens to effect this would facilitate at times the resolution of a "line" into its component dots. The general rendering of an object would be deleteriously effected by such a procedure, but in certain cases distinct advantages might be gained.

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ILLUMINATION IN MICRO-METALLOGRAPHY.

By Henry M. Sayers.

In discussing this subject before this audience it is only necessary to set out certain propositions as assumed and accepted to give form and cohesion to the whole treatment. These assumed propositions are as follows:—

1. Correct illumination is essential to obtain the best results of which the objectives and oculars used are capable.

2. The principles of correct illumination are the same for the examination of opaque objects such as those studied in metallography and that of the (partially) transparent objects examined by transmitted light.

3. The illumination which permits of the utilisation of the maximum potential resolving and defining power of any objective is given by an image of the source of light projected on to the object, formed by cones of light with apex angles approximating to the angular aperture of the objective in the medium used.

4. Micro-metallography implies the use of the highest optical power available—though not necessarily in every case—and the use of photographic records.

5. Micro-metallography implies the use of some form of "vertical illuminator," and of the objective as a condenser, in all but quite low-power work.

6. It is desirable to shorten photographic exposures as much as possible, especially at high magnifications, and to avoid "glare" which reduces contrast and obscures fine detail.

7. The present effective magnification has an upper limit of about 1,000 diams., due to the limitation of the N.A. of objectives to a maximum of about 1.4 by the optical constants of the glasses and immersion media available. Any increase in N.A. and effective magnification will require a corresponding increase in illumination efficiency.

Proposition 5 sets out two conditions which constitute important differences in the application of correct illumination to opaque and to transparent objects, and give rise to the principal difficulties in attaining good illumination in metallography. The vertical illuminator entails a great loss of light. The use of the objective as the condenser also entails limitations which do not arise in the same degree when these two components of the optical system are independent.

If a total reflection prism is used as the vertical illuminator it may reflect nearly 100 per cent. of the light falling on it into the objective, but it intercepts all the light from the objective passing towards the image plane which falls on it. In the best case the prism occupies half the objective aperture, only half the objective receives light from it, and half the light going to the image is intercepted. Hence only 25 per cent. of the illuminating beam can be utilised in the image. If the prism is either larger or smaller the percentage of light getting through to the image is less than 25 per cent.

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Similarly, if a cover-glass type of reflector is used the maximum illumination possible theoretically would be given if the reflector reflected 50 per cent. of the light and transmitted 50 per cent. The result would be 25 per cent. of the light utilised. No cover-glass type reflector does nearly so well as this. Measurements of a clear cover-glass have given me a reflective power of 13.8 per cent. compared with a silvered total reflection prism, and a transmission of 66 per cent., with the glass inclined at 45° to the beam. The resultant for the image illumination is therefore 13.8 × 66 per cent. or 9.2 per cent. for the image. A semi-platinised cover-glass (not made for the purpose) gave 38 per cent. reflection, but only 21.5 per cent. transmission or 8.17 per cent. for the image. The light, too, was brownish yellow.

The prism reflector, while much superior to the cover-glass in respect to illumination, cuts down the effective aperture of the objective, both as a condenser and as an objective, and does this unsymmetrically to the detriment of its resolving power. This is probably the reason why prism reflectors are never made to cover nearly so much as half the objective aperture, and they are consequently not in practice much better than cover-glasses in respect to brightness of image.

The diminution of light intensity in the image compared with that reflected by the object is proportional to the square of the lineal magnification, increased by absorption and reflection in the optical system. With 100 diameters the light intensity at the image is under one ten-thousandth, and with 1,000 diameters under one-millionth part of the light reflected by the object. Allowing for the loss due to the vertical reflector it is for the two magnifications mentioned less than one forty-thousandth and one four-millionth part respectively of the light intensity of the source for any part of the object which has perfect reflecting power, assuming that the image of the source is as bright as the source itself. As these small fractions are on assumptions of 100 per cent. efficiency for every stage of reflection and refraction between the source and the image, which is unattainable everywhere, it may be roughly estimated that the actual fractions of the source brightness in the brightest points of the image will be more nearly one ten-thousandth and one ten-millionth respectively. The most obvious improvement would be the devising of a vertical reflector giving an efficiency of combined reflection and transmission approximating to 25 per cent. without cutting down the objective aperture.

The exposure required is that for the " shadows " of the object, *i.e.*, for the darkest parts which show perceptible detail. It follows that to get reasonable exposure times only light sources of great intrinsic brilliancy are of practical use for photographic work. The total candle-power of the radiant is no criterion by itself, it is candle-power per unit area of radiating surface which counts.

Of the available sources the positive crater of the carbon arc is the most brilliant. After that come in descending order the Nernst lamp, the tungsten arc (or Pointolite), the half-watt metal filament lamp, and the oxy-hydrogen lime-light. The last named is the only light source depending on combustion at all suitable for the purpose,

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but it requires cumbersome accessories and so much attention that it need hardly be considered unless an electric supply is quite out of reach.

The mercury vapour lamp ought to be mentioned, but the writer has no experience of it, can find no information as to its intrinsic brilliancy, and has seen no form of the lamp which is convenient for metallography. The nearly monochromatic quality of the light is in its favour, and it is probably capable of being put into a very useful and efficient shape for the purpose.

The arc crater gives the highest light intensity. With the requisite attention it is unsurpassable in rapidity and quality of negatives. But it has some disadvantages. The positive crater is somewhat obscured by the tip of the negative carbon, the crater surface is not always of uniform brilliancy all over, and the crater may shift during an exposure from one part of the carbon to another. Such unsteadiness may arise from the arc length being too great from an endeavour to get the negative tip out of the field of view; from impurities in the carbons, or from draughts. The arc length has to be adjusted at intervals of a few minutes. The arc does not steady down until it has been burning for several minutes. It is therefore an item of the equipment to be attended to and waited on. The arc gives off a large amount of radiant heat which has to be considered in relation to any auxiliary lens system required. It therefore leaves something to be desired in point of convenience and its rapidity in photographing is subject to some discount for the time taken in attending to it.

The Nernst lamp is excellent in many ways. It requires no globe, no attention, and is quite steady. It gives off relatively little radiant heat. It can be used on either continuous or alternating current. The shape of the radiant surface, a rod of quite small diameter is somewhat inconvenient, as it calls for very accurate centering of any auxiliary lens system. It has been unobtainable in this country for some years, as it is made only in Germany. The small diameter of the rod obliges one to magnify it considerably by the auxiliary lens system used, so that the effective brilliancy is not so great as might appear. With a one-ampere Nernst lamp I have done a good deal of work on steel at 700 to 1,000 diameters, and find the exposure required to be from five to ten minutes at such powers, using fast plates and a light filter.

The Pointolite or tungsten arc is free from the inconveniences of the carbon arc. The source of the light is a small ball of tungsten which appears in the field of view as a disc of uniform brilliancy fixed in position. Its intrinsic brilliancy from some rough tests of my own seems to be about one-third that of the carbon arc crater. It lights up at once, is normal in a few seconds, requires no adjustment or attention, and gives off a relatively small amount of radiant heat. It is very promising and the larger sizes which are being developed may prove to be as quick in work as the carbon arc, when the absence of attention and unsteadiness are taken into account. Like the carbon arc, it requires continuous current for its operation.

Half-watt lamps with straight filaments as made for motor-car head lights are quite useful. Their intrinsic brilliancy is little inferior to that of the tungsten arc. The small diameter of the coiled filament is open to the same objection as the Nernst filament, *i.e.*, it has to be

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much magnified to fill the field of view, so that the effective brilliancy is reduced. Moreover the separate turns of the spiral become visible in a critical image. These small lamps can be run from a few ignition cells, so that they are convenient for portable use. Run from an ordinary supply circuit they require either a resistance or a transformer to reduce the pressure to 6 or 8 volts. Good work has been done at high powers on steel with a 6-volt 4-ampere half-watt lamp, but the exposure is two to three times as great as with a Nernst lamp. Up to 150 diameters this exposure is reckoned in seconds, so the difference is not important, but for high powers the exposure goes up to several minutes (15 to 20), it counts where much work has to be done. Long exposures are objectionable not only because they limit the speed of work, but also because they increase the risk of disturbance of the image by vibration.

The illuminations needed to give short exposures are far too bright for comfort in visual examination. The interposition of a piece of fine-grained ground glass is a simple remedy. It can be put anywhere between the light source and the vertical reflector and no adjustment is disturbed. The final focussing must be done on the ground glass of the camera, where the full illumination will not be found excessive for the purpose.

Anyone starting on micro-metallography will find his initiation much easier if he tries first visual and photographic work by transmitted light on transparent objects. As the sub-stage condenser is independent of the objective it is much easier to try variations of focus and illumination, and the knowledge so gained helps very much to recognise proper and improper condition in opaque work. Good objects for such training are section of Echinus spine for low powers, and diatoms of various fineness of structure for the higher ones. A student who can get a good dark round negative of Echinus spine at 100 diameters, and good " black-dot " negatives of Pleurosigma Angulatum or Surirella Gemma at 1,000 diameters with an oil immersion objective will find work on metals much simpler than if he came to it without such practice. The superior resolving power and definition of a given objective with the sharp image of the illuminant focussed on the object from a sub-stage condenser of aperture comparable to that of the objective will be appreciated.

In metallography (excepting with the very low powers) the objective plays the part of the sub-stage condenser as well as its own. To obtain a sharp image of the source of light upon the object when the object is focussed to the eye-piece, certain distance relations between the illuminant, the objective, the object, and the image plane must be observed. They are simple. The light source must be at the same distance from the back lens of the objective as the image plane, the distances being measured along the path of the light in each case Obviously the source and its image on the object are at the conjugate focii of the objective; and the object and its image are at equal conjugate focii. An immediate consequence of this relation is that the illuminated field or useful part of the image formed by the objective is of the same dimensions as the source (real or virtual) of light itself. If, for example, the source of light is the crater of an arc, one-tenth of an inch in diameter, the usefully illuminated part of the real image

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formed by the objective will also be one-tenth of an inch in diameter. This identity of dimensions is independent of the power of the objective. A two-third inch with a power of 8 and a one-twelfth inch with a power of 100 with both give an illuminated circle of one-tenth inch diameter in the image plane, provided that the conditions of critical illumination are observed. If the total magnification on the camera screen is ten times the objective image magnification, the effective field will be one inch in diameter. This is generally too small for practical use, and is much smaller than the field which the objective can cover. One wants a field at least three inches in diameter to cover a quarter plate. The assumed magnification of ten due to the ocular and camera length combined is about as much as the best objectives will usefully stand. So that to cover a quarter plate the radiant should be from a third to a half inch in diameter.

Unfortunately the available sources of light are of small area. An arc crater of a quarter-of-an-inch diameter corresponds to an arc current of 30 to 40 amperes, and is not really large enough. As the crater diameter increases only as the square root of the current, one would require a searchlight arc, with many tens of amperes to give a crater three-quarters of an inch in diameter, which is about the ideal size to fill an eye-piece. Such an arc is not practicable. Even a 40 ampere arc gives out too much radiant heat to be brought within the few inches of the microscope corresponding to the posterior focus of the objective. The same difficulty of small area is true of the other available sources. The 100 candle-power Pointolite has a radiant surface about one-tenth of an inch diameter. The Nernst and half-watt lamps have filaments of much smaller diameter. There seems no good reason why a half-watt spiral lamp filament should not be made one-third or one half-inch diameter. There may be manufacturing difficulties, or it may be that the makers have not seen that there is any use for such lamps. If made the spiral, or rather helix should be flattened to bring the radiant surface as nearly as possible into a plane.

The actual radiant surface therefore has to be magnified in some way to give a field of sufficient area. The simplest way is to use a short focus condenser to project near the upper lens of the objective an image of the radiant. This can be focussed on to the stop of the vertical illuminator, and the fine focussing done by eye. The image thrown on the object is that of the aperture of the condensing lens which is then at the posterior focus of the objective. A condenser of the Nelson type of two inches full diameter, stopped down to one inch aperture works well. It must be carefully centered to the radiant, and both must lie on a line at right angles to the optical axis of the microscope. To make these adjustments readily, some form of mounting equivalent to an optical bench, with vertical and horizontal movements to either the lamp or the lens is necessary. If the lens is always used for the same stand, it can be fixed at the height of the optical axis, and the adjustments for centering made on the lamp carrier. Movement to and from the microscope to adjust the lens distance to the optical tube length in use—which may be different with different combinations of objectives and oculars—and some movement parallel to the body to allow for the range of movement of the illuminator aperture, are necessary. These statements hold true for any of the auxiliary arrangements described.

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The condenser must be of short focus in order to take in a large cone of light from the radiant. The Nelson condenser mentioned has a working distance of about one-and-a-half inches. This is too short for an arc of even ten amperes, but with a Nernst or half-watt lamp up to 100 candle power the heat will not injure it. The Pointolite lamp of 100 candle power has a bulb which is just too large for such a condenser to focus at the required distance.

Another arrangement is to set up a screen with an aperture of the required size, say seven-eighths inch to one inch, which may conveniently be an iris, at the required distance and to throw on that aperture a magnified image of the radiant. The image formed by the objective on the object will then be a reduced one of the radiant. This arrangement takes up a good deal of room. Thus if the aperture is one inch in diameter and the radiant quarter-inch diameter, and a lens of four inches focal length is used, the total distance from the microscope body will be from 32 to 36 inches, which is awkward for making the adjustments, attention to the arc, etc. It is doubtful whether a lens of four inches focal length could be safely used with an arc giving a quarter-inch diameter crater. A six-inch or eight-inch focus would probably be required and proportionately more distance occupied. It follows that there is not really much advantage in using radiants larger than those which permit of the use of lenses of about two inches focus. More light is produced, but no more is utilised.

A third method is to present to the objective a virtual image of the radiant, *i.e.*, to use an auxiliary lens as a simple magnifier, the objective taking the place of the eye. The focal length difficulty comes in again, as the lens must be closer to the radiant than its focal length. A lens combination with its equivalent plane well in front of it, so that the working distance from the radiant is greater than the focal length, gets over this. Such a combination which I have used with success is a Nelson condenser with a flint concave between it and the microscope. The combination is really a microscope of the Brucke type. The concave is placed close up to the aperture of the vertical illuminator, and focussed by moving the radiant to or from it. As the radiant and condensing combination are both within a few inches of the microscope body, adjustments are easily made while observing the object. The image given by the objective is a real image of the radiant. The magnification may easily be ten times.

Whatever arrangement is used there should be provision for interposing a ground glass or light filter in the path of the beam. For metallography a light filter is not needed for securing contrast as in stained specimens photographed by transmitted light, but for cutting out the chromatic residuals given by even the best objectives. The sharpest visual focussing on the camera screen without a filter fails to give an equally sharp negative. A green filter, such as the F line filter, or a malachite green gives sharper results without a great increase in exposure.

With either of the two first named auxiliary arrangements a glass micrometer can be placed in the focal plane which is the virtual radiant and the scale image focussed on the specimen can be photographed at the same time. This is equivalent to an eye-piece micrometer. Its size on the camera screen is a measure of the magnification

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due to the ocular and camera length. Like any eye-piece micrometer, its actual value needs to be calibrated against a stage micrometer, but it is available with any eye-piece.

There remains the difficulty of "glare." The worst source of this trouble is reflection from the surfaces of the objective lenses. The upper convex surfaces are the strongest reflectors. Fortunately the condition that the illuminating beam should fall as if it proceeded from the image plane, means that it is made up of divergent rays which a convex reflector cannot bring to a focus, but reflects with an increased divergence. Consequently with the light focussed correctly only a small spot of glare light appears at the apex of the upper objective lens. The bulk of the reflected light is scattered to the tube sides. Obviously the objective mount and body tube should be well blacked inside. Reflections from the inside of lamp bulbs and other stray light may give trouble. It is best to keep all these away by a screen, which may be the mount of the auxiliary lens or aperture. Another source of glare is reflection from the front lens of the objective. It is only troublesome with dry objectives of short working distance. With those of 2/3 inch and over it is not serious, but it is hardly possible to get negatives with good contrast with dry objectives of 1/4 or 1/6 inch. Perhaps this is one reason for the fact that very little metal work is done at magnifications between 150 diameters, the upper limit of a 2/3 inch or 16 mm. objective, and 700 diameters corresponding to a 1/12 inch or 2 mm. oil immersion. One can, of course, get intermediate magnifications by using low ocular and camera length with an oil immersion, but the field covered is too small for the general view required. The Zeiss 3½ mm. or 1/7 inch oil immersion fills the gap very well. I have tried to get English firms to make a similar lens, and one maker listed a 1/6 inch oil immersion for metallurgical purposes before the war, but has ceased to make it. I would suggest that a 6 mm. or 8 mm. oil immersion should be made for the work. The working distance need not be too great for the oil contact, no cover glass has to be allowed for, conditions favourable to giving the objective a relatively large N.A. without introducing specially great manufacturing difficulties. The Zeiss lens mentioned was quite cheap, and of excellent performance. A one inch or 2/3 inch of about .30 N.A., a 1/3 or 1/4 inch oil immersion of about .70 N.A., and a 1/12 inch of 1.3 to 1.4 N.A. would furnish a metallographer with a battery serving all the purposes.

For low power work there is room to put the vertical illuminator below the objective, and it can be arranged to give either vertical or oblique light. Even here it will be found advantageous to use an image of the radiant formed by an auxiliary lens.

To sum up the above, it may be said that the items in which improvement is desirable are the following:—

1. A transparent vertical illuminator which shall get nearer the theoretical perfection of reflecting 50 per cent. and transmitting 50 per cent. of the light incident on it at 45°, without colouring the transmitted light. Optically worked glass lightly platinised seems the most promising.

2. A light source of uniform and steady high brilliancy presenting an area of half-an-inch square or a little more, to which a condenser of 2 inch working distance can be focussed without damage from

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radiant heat. Either the half-watt or the Pointolite lamp may be able to meet this. The limitation of bulb size is important.

3. Oil immersion objectives intermediate in focal length and aperture between the 2/3 inch and the 1/12 inch, well corrected for colour. If anything can be done to reduce glare from internal reflection in the objectives designed for metallography it will be an advantage.

4. An auxiliary condenser combination with a long working distance compared with its focal length to be used to present a magnified virtual image of the radiant to the objective. Suitable specification would be:—

Focal length, 1½ inches to 2 inches.
Working distance—anterior—3 inches to 4 inches.
Clear aperture, ¾ inch to 1 inch.
Well corrected spherically and chromatically.
Mounted with a flange or a flanged collar.
Cost reasonable.

5. A simple firm optical bench or geometric slide arrangement with carriers for lamp and condenser at heights corresponding to those of usual microscopic axes when in the horizontal and vertical positions. The whole bench or slide to be capable of movement parallel to the microscope axis for 2 or 3 inches.

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THE USE AND NEED OF THE MICROSCOPE IN ENGINEERING WORKS.

By S. Whyte, B.Sc.

It is not necessary in these days to set out in detail the practical help which is derived from the use of the microscope in engineering. Everyone knows the great benefit it has been in controlling the question of steel supplies and their heat treatment. By its means inherent defects in the steel are discovered. Troubles may arise at the steel works through bad ingot pouring, and any pipes or seams which occur in the portion of the ingot which is used finds its way into the billets and bars. Also, faults may arise in the forging or stamping of the steel which are difficult to detect without a microscope. For finished parts the microscope is almost essential in working out and standardising the best methods of heat-treatment, and in the event of failures of these parts in service, in helping to discover the processes by which these failures originate and develop. This by no means exhausts the list of uses to which the microscope can be applied in examination of metals for engineering works, as the properties of castings—both ferrous and non-ferrous—can be co-related with their various micro-constituents and their distribution or crystalline arrangement.

The writer does not propose dealing in detail with the various branches in which, from his own experience, he has found the microscope to be of great value. It is sufficient to say in passing that the microscope ought to be, and will be in the near future, an essential part of the average engineering works equipment, especially where the products being manufactured are subjected to live loads, and on which the safety of life depends.

The purposes for which the microscope is used, as outlined above, are three-fold, and endless examples could be given.

First, in the examination of raw material, as supplied by the steel makers and stampers. It is not enough in all cases to buy merely to chemical specifications, as two pieces giving the same analysis may differ in their usefulness. One may be sound, while the other shows segregations and results of ingot piping. Faults such as these, however, are becoming rare, as the improvements in recent years, specially in regard to ingot casting, have done much to eliminate them. It is, however, still important that samples of new types of stampings, as they come from the makers, should be examined for incipient cracks or "laps" of oxide driven into the material, specially when the stampings are intricate, and the steels used are alloy steels. It is impossible to tell, other than by the microscope, that some of these flaws exist, and it will help the stamper to correct his dies, and will save time and expense and the possibility of subsequent failures from this cause, if defects can be detected from the beginning. Micro. No. I. is an example of this type of defect.

Secondly, and what is more important from the engineer's point of view, the microscope is a great help in arriving at the best heat-treatment temperatures for his steel. It is absurd to buy expensive high-grade alloy steels, and not use every means of obtaining the best results from them. It is equally extravagant to buy high-speed steel for tools

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and waste it, and much time in the machine shop, through bad hardening. For machine parts, pyrometers and testing machines are necessary in standardising methods after the temperatures have been established, but with high-speed steel, where the hardening temperatures are usually high, the recording of these temperatures is not so reliable and calls for all the more precaution in testing the conditions by micro-examination of the steel after hardening. Micros. Nos. II. and III. show the structure of an 18 per cent. tungsten steel heated to a satisfactory temperature, and overheated, respectively. The overheated, or burnt structure of No. III., shows the large crystals of austenite with oxide beginning to form round their boundaries. On the other hand, the best cutting properties of the steel are not brought out unless the steel is heated to a temperature high enough to diffuse all the free iron tungstide, which is present in the annealed condition. Micro. No. IV. shows the same high speed steel where the hardening temperature has not been high enough or the time of soaking not long enough, and too much free tungstide is still present.

Thirdly, and most important for the engineer, is the use of the microscope in helping to locate the causes of failures, and in working out the processes by which these fractures develop. The causes of failure are numerous, and apart from those due to inherent defects in the steel as mentioned above, the principal one is that of " fatigue." In " fatigue " fractures, the origin is usually found in a weakness of design or in using steel of too low an elastic limit. Sometimes a piece of non-elastic slag, occuring at a point of maximum stress, sets up local stresses high enough to start a fracture. In designing machines, a radius replaces a sharp corner whenever possible, when working stresses are set up at these points, so that the stresses shall be distributed as evenly as possible. Sometimes one finds an accidental notch, such as a file mark. in a radius, which sets up a " fatigue " fracture. An example of this may be given, as it brings out points in connection with the microscope objectives, which appear to be worthy of consideration. Micro. No. V. shows such a V-notch, accidentally made by a file in the radius at the foot of a stop in a machine gun lock mechanism, which received rapidly repeated blows. The notch has concentrated the stresses to such an extent that overstraining of the material has taken place, and a crack is seen originating at the apex of the notch. The crack, as it develops, is seen to be deflected through a slag inclusion, Micro. No. VI., and in other places in the same specimen it was noticed that " strain picture " was highly developed round these slag inclusions, although fracture had not commenced.

In microphotograph No. VII. this strain structure is also seen around the end of the crack which had penetrated about 1-16 in.

It is in cases such as the above that good objectives are necessary, and more so when alloy steels are being examined. In non-ferrous metals the crystal grains are usually much larger, and strain structure is easily resolved with comparatively low magnifications. Microphotograph No. VIII. shows a brass which had been strained during machining.

It is in photographing the fine-grained steels that the differences in the microscope objectives show up. In photographing Micro. No. VII. the secondary spectrum of the achromats would give bad definition but, with the elimination of this in the apochromats, by the union

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of three colours of the spectrum at one point instead of two in the achromats, a great improvement is effected. This, with the correction for spherical aberration in two colours, gives an image of greater sharpness for either white or monochromatic light.

For low power work, however, and for certain subjects on higher power work, a flatter field and better results can often be obtained by achromatic objectives, as the larger aperture of the apochromats tends to give a slight curvature of the image, which even the compensating or projection ocular cannot entirely correct.

At the same time it is felt that even the best made German objectives do not give enough magnification for micro-photography, as the very fine structure of some alloy steels are at present most difficult to resolve, and much that is now impossible to see might be brought out under higher magnifications. Microphotographs Nos. IX. and X. show "etch figures" in crystals of pure nickel. These serve to determine the crystalline system to which nickel belongs. The crystal in Photograph No. IX. shows a twinning plane, and the consequent difference of orientation as shown by the "etching pits." It is impossible to say what internal structures might be brought out in heat-treated alloy steels by higher magnifications, as the crystal grains are so much smaller than those of the nickel shown in Photographs IX. and X.

For metallographic work the following provisions on the microscope seem, to the writer, to be advisable for good work. The microscope should be usable in the horizontal position.

The stage should have a mechanical movement in two directions, at right angles to each other. The stage should also have a racking motion for focussing, as it is usually more suitable to rough focus by this means in preference to that on the tube, as it does away with the necessity of altering the position of the optical bench. The fine adjustment is usually on the tube of the microscope, and this is the most convenient place.

Ordinary Huygenian eye-pieces are most suitable for achromatic objectives, while for the apochromatic objectives special compensating eye-pieces are necessary. For photography a projection eye-piece gives the best results.

The disc illuminator gives most satisfactory results and, with a diaphragm between it and the source of light, good definition can be obtained.

The objectives as mentioned previously should be used according to the subject—the achromats give every satisfaction for the general run of metallurgical work and, even in photography, are often preferable to the apochromats, by giving a flatter field. However, when photographic records of very fine detail are desired there is no doubt of the superiority of the apochromats for the purpose.

It seems to be desirable to be able to obtain much higher magnifications than are at present obtainable by the present objectives, but, in all probability, improvements in the methods of polishing the specimens will also have to be developed to secure a surface good enough to bear the higher magnification.

There is undoubtedly a great future before the microscope in its application to engineering work, in relation to designs, steel and its heat-treatment.

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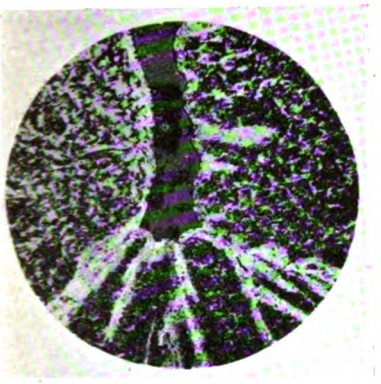

FIG. 1.

Spec.: Small Forging.
Illum.: Vertical.
Camera: 66 cms. Obj.: 20 mm.
Ocu.: Projn. Mag.: 90 diams.
Etched: Picric Acid.
Remarks: Slag driven into steel along with some decarbonised layers from the surface. .42% C. steel.

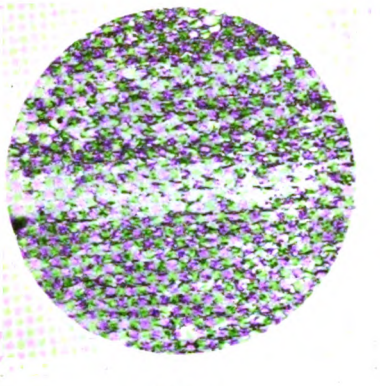

FIG. 2.

Spec.: High-speed Steel.
Illum.: Vertical.
Camera: 78 cms. Obj.: 4 mm.
Ocu.: Projn. Mag.: 500 diams.
Etched: Picric Acid.
Remarks: Fine Grains of Austenite with traces of free tungstede steel unabsorbed. (White globules.)

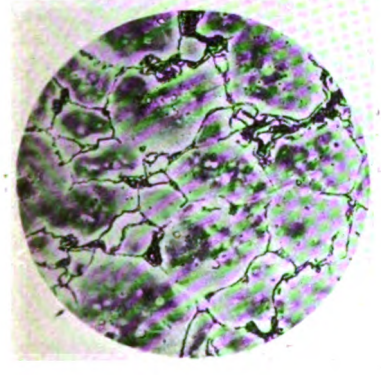

FIG. 3.

Spec.: High-speed Steel.
Illum.: Vertical.
Camera: 66 cms. Obj.: 2 mm.
Ocu.: Projn. Mag.: 1,000 diams.
Etched: Picric Acid.
Remarks: Large grains of Austenite surrounded by oxide.

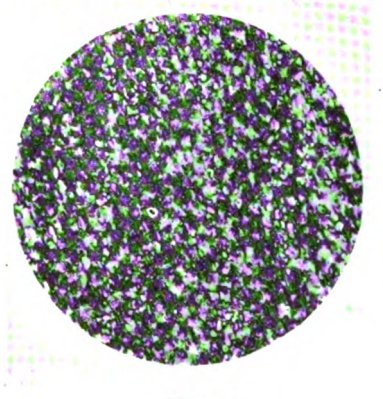

FIG. 4.

Spec.: High-speed Steel.
Illum.: Vertical.
Camera: 78 cms. Obj.: 4 mm.
Ocu.: Projn. Mag.: 500 diams.
Etched: Picric Acid.
Remarks: Fine grains of Austenite with considerable amount of free tungstede. (White globules.)

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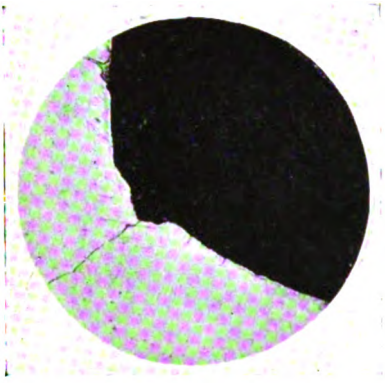

FIG. 5.

Spec.: Machine Gun Mechanism.
Illum.: Vertical.
Camera: 78 cms. Obj.: 4 mm.
Ocu.: Projn. Mag.: 500 diams.
Unetched.
Remarks; File mark in radius at bottom of extractor stop.

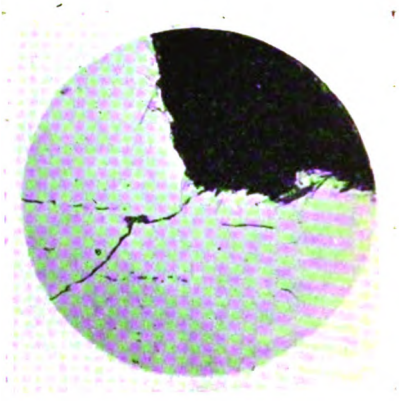

FIG. 6.

Spec.: Machine Gun Mechanism.
Illum.: Vertical.
Camera.: 61 cms. Obj.: 2 mm.
Ocu.: Projn. Mag.: 1,000 diams.
Unetched.
Remarks: File mark in radius deflected alongside slag patch.

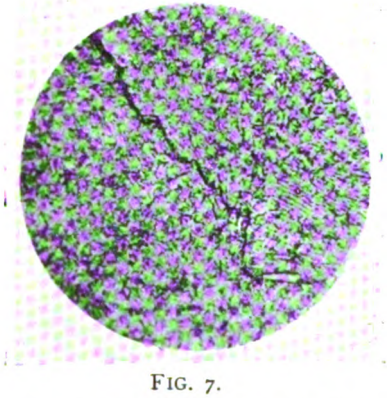

FIG. 7.

Spec.: Machine Gun Mechanism.
Illum.: Vertical.
Camera: 92.5 cms. Obj.: 2 mm.
Ocu.: Projn. Mag.: 1,500 diams.
Etched: Picric Acid.
Remarks: Strain in structure round crack in .50% C. steel. Troostitic condition.

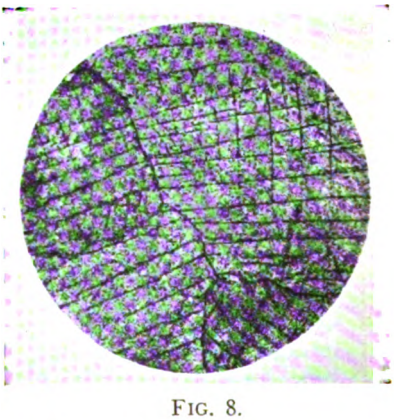

FIG. 8.

Spec.: B. Brass.
Illum.: Vertical.
Camera: 55 cms. Obj.: 4 mm.
Ocu.: Projn. Mag.: 250 diams.
Etched: Ammonium hydrate.
Remarks: Shows junction of three crystal grains. Each with own system of slip bands.

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FIG. 9.

Spec.: Nickel Rolled Bar.
Illum.: Vertical.
Camera: 92.5 cms. Obj.: 2 mm.
Ocu.: Projn. Mag.: 1,500 diams.
Etched: Nitric Acid.
Remarks: Etching pits in nickel crystals.

FIG. 10.

Spec.: Nickel Rolled Bar.
Illum.: Vertical.
Camera: 92.5 cms. Obj.: 2 mm.
Ocu.: Projn. Mag.: 1,500 diams.
Etched: Nitric Acid.
Remarks: Twinning plane in nickel crystal with resulting difference in orientation.

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SUGGESTED IMPROVEMENTS IN THE METALLURGICAL MICROSCOPE

By Professor H. Le Chatelier (*Paris*).

The writer has for some considerable time been endeavouring to extend the use of the Microscope in Metallurgical Works. No one to-day will contest the services that Metallography renders to Industry, and it is possible that the sphere of usefulness of this method of investigation could be still further extended by improvements in detail.

The object of this brief note is to point out two possible improvements.

In the first case, to obtain good photomicrographs the use of apochromatic objectives is necessary. These are very costly and many workers hesitate to incur the expense of providing them. Would it not be possible to persuade Manufacturers to design Objectives corrected for some single wave-length of the spectrum?—viz., the blue line of the Mercury Vapour Lamp, which is easily separated from the other rays and which moreover has a considerable actinic effect. Such simple objectives in which it would only be necessary to take into account corrections for spherical aberration could be manufactured as a single lens and would thus be comparatively cheap.

The second improvement, which it is desirable to introduce into an objective used for the examination of metals is to give to the radius of curvature of the back surface such a value as to prevent concentration of the light reflected from this surface. In all Metallurgical Microscopes illumination must necessarily be effected through the objective. This is a new condition and consequently one complication more in the construction of objectives, but perhaps it may not be insuperable.

From an entirely opposite point of view it would be very useful if a small handbook were drawn up for the use of those who employ the Microscope, as well as for a few of the Manufacturers, such a manual explaining the essential properties of the instrument. Every day the grossest errors are made in this connection. A great number of experimenters imagine that a Microscope Objective can be used like a thin lens. They forget that every objective is constructed to give an image at a fixed point, this being 16 or 25 centimetres according to the country of manufacture. We frequently see photographs taken with a Microscope objective, in which the adjustment (tube length) is changed so as to project the image a greater or lesser distance according to the magnification it is desired to obtain. Now, on the contrary, the extension of the Microscope should always remain invariable and a projection eye-piece used for taking the photomicrograph. The distance of the two lenses of this eye-piece should be adjusted according to the magnification desired.

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Another practice which should be no less condemned when using the Metallurgical Microscope is that of reflecting the luminous pencil at right angles by means of a total reflection prism placed in the path of the pencil of light, instead of employing a silvered reflecting mirror. The former method completely changes the working of an objective by making the pencil of rays pass through a piece of glass many centimetres thick. The objective is calculated for working in air and not in glass.

These errors are not very important when the examination is simply by the naked eye, because the eye has an extraordinarily high degree of accommodation. This, however, is not the case in photography. Frequently the sharpness of image that ought to be possible where objectives are properly used is far from being obtained.

To sum up: hitherto Microscopes have only been seriously investigated for the examination of transparent objects and it would be highly desirable if this study could be resumed and extended with a view to the examination, by reflection, of polished opaque bodies like metals.

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SUGGESTED ALTERATIONS IN THE DESIGN OF THE LE CHATELIER TYPE OF METALLURGICAL MICROSCOPE,

By Professor F. Giolitti (*Italy*).

It is well known that the principles laid down by Le Chatelier for the design of his instrument have been applied, with different constructional details, by various Makers and it is also recognised that the design of the Le Chatelier Microscope which has found greatest favour is that adopted by Pellin of Paris and Dujardin of Düsseldorf.

I have had long and practical experience of this latter type of design, and I do not think I am wrong in stating that, even though the Le Chatelier Microscope offers the best solution of problems connected with the microscopic examination of metals, and is much preferable to all similar types of apparatus on the market, it has two disadvantages, which, however, are quite easy to rectify by means of some simple modifications in constructional detail.

The first of these disadvantages consists in the fact that the rack which supports the stage is directly fixed " on one side " of the stage, so that the weight of the stage and of the object placed upon it tends to produce a sagging of the rack.

This sagging effect becomes more and more pronounced as time goes on, and prevents the focussing of the whole of the metallic section under examination. It is intensified, and in a short time may seriously damage the instrument when it is required to examine fairly heavy specimens, and this is a case which frequently occurs in practice.

The second disadvantage consists in the absence of an apparatus, which, like the revolving objective holder in the ordinary Microscope, permits of rapidly and easily changing the objective. In the Le Chatelier instrument, in order to change the objective, it is necessary to raise the stage, unscrew the first objective, screw the second objective into the place of the first, lower the stage, and refocus. This operation is very long and tedious, and it is even more so when, with a view to preventing the inconvenience of allowing the various objectives to remain uncovered on the work table, it is necessary each time to put back into its case the objective which has been removed from the Microscope and take out of its box and fix on the instrument the new one required. And, of course, it is often necessary to examine each metallic section under various magnifications, in order to find out with accuracy the true significance of the various structural elements, and eliminate errors in the interpretation of the structure.

For these reasons I have studied, with the help of Dr. A. Filippini of Genoa (to whom I extend my heartiest thanks for his valuable collaboration), a type of Microscope which, while still preserving the extremely useful fundamental principle of the " vertical " observation which makes the Le Chatelier Microscope so practical, gets over the disadvantages to which I have referred.

The new Instrument differs from similar apparatus principally by the addition and different arrangement of a few of the external parts, which are clearly shown in the illustration, Fig. 1.

I will, therefore, only refer very briefly to the features of these parts, without touching upon anything regarding the other components of the Microscope—such as method of illumination, system of projection, etc.—which do not differ essentially (except for the special

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design rendered necessary owing to the new type of construction) from the corresponding parts of other similar apparatus.

As is clearly shown in the illustration, in the new instrument I have endeavoured to eliminate the first of the two disadvantages mentioned, by supporting the stage by a bar fixed to it at two opposite points. The bar is, in its turn, supported by the rack, the axis of which coincides with the perpendicular of the stage, carried through the centre of the stage itself. It is evident that in this way the defects due to the sagging of the rack are eliminated, provided care is taken in centreing the objects to be examined in the middle of the stage.

In the instrument constructed by Messrs. Reichert it is possible to support on the stage specimens weighing several kilogrammes, without any appreciable deviation from the normal between the optical axis and the plane of the polished surface resting on the stage.

Owing to the frequency of cases in which in practice it is necessary to place very heavy objects on to the stage, I have thought it necessary to take the weight of the object off the fine focussing micrometer screw, by fixing—as will be seen in the photograph—the screw itself to the slide which carries the tubes of the visual and projecting eye-pieces. The result is that the coarse movements and approximate focussing are effected by moving the stage, while the comparatively delicate movements required for very fine focussing are made by manipulating the eyepiece tubes. It will be recognised, owing to the smallness of the movements necessary to bring the objects into correct focus, that such a modification does not detract from the proper illumination of the object.

I have overcome the second disadvantage mentioned by adding to the microscope a proper revolving holder for 4 objectives. The use of the revolving holder offers some difficulties in this case; both owing to the necessity for fitting it in such a way as not to hamper the various functions of other components of the instrument, and with a view to preventing any modification in the characteristic dimensions of the objectives by deviating from those which give the best results in the examination of opaque metallic specimens illuminated by reflected light. The first difficulty has been overcome by replacing obliquely the bar which supports the stage, in the manner shown in the photograph. The second difficulty has been eliminated by giving to the revolving objective holder the special shape represented in the same illustration.

The above description refers to the design of instrument for visual observation. The complete apparatus as used for Photomicrography is shown in Fig. 2.

In addition to the advantages mentioned above, the new Microscope offers still another—not indispensable—of permitting the oblique illumination of the specimen examined with the low power objectives. The adjustment for oblique lighting, which already existed in the Metallurgical Microscope designed by Martin, had to be abandoned, from considerations of manufacture, in that of Le Chatelier, but it has been satisfactorily applied in the new instrument, thanks to the special design of its essential parts.

For the reasons already referred to, it is unnecessary for me to describe the new instrument in more detail. I would only add that in practical application the features of design which I have briefly outlined above have shown themselves to be extremely useful.

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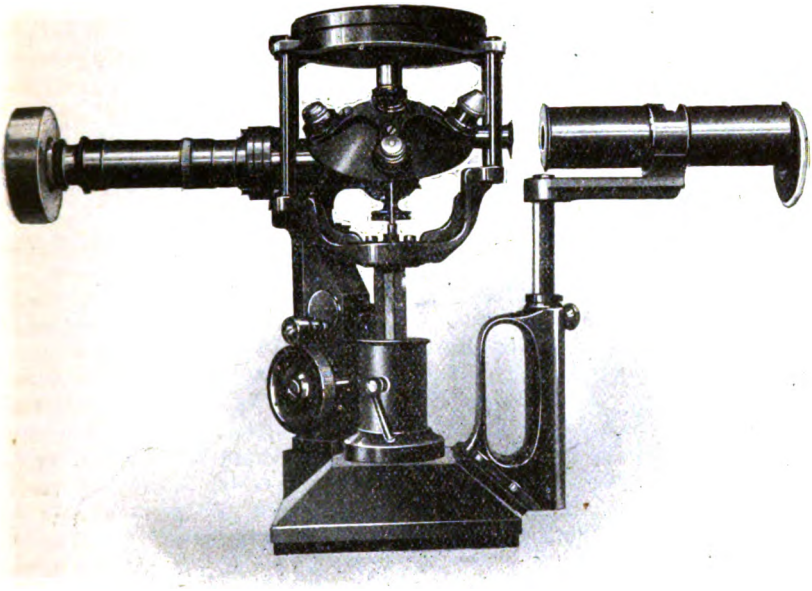

FIG. 1.

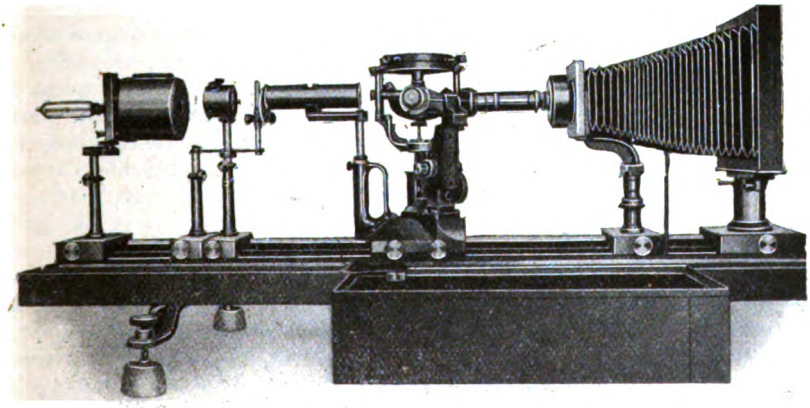

FIG. 2.

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IMPROVEMENTS IN METALLURGICAL MICROSCOPES.

By Albert Sauveur (Harvard University).

At the kind request of Sir Robert Hadfield, I am submitting this slight contribution to the symposium on the microscope and its applications. Referring first to the minor improvements I have been able to introduce into the construction of metallurgical microscopes, I venture to mention the following points.

It is, I believe, at my suggestion that microscopes for metallurgical work were first constructed by the Bausch and Lomb Optical Company, of Rochester, New York, with a stage that could be racked up and down in a manner similar to the substage attachment, thus affording greater working distance, and doing away with the necessity of ever having to displace the vertical illuminator, the condensing train and the source of light as objectives of varying focal lengths are used. It is also at my suggestion that in inverted microscopes and in the vertical-horizontal type herewith illustrated a totally reflecting prism was attached to a horizontal draw tube, affording a ready means of pushing it in or drawing out of position as desired.

The two types of metallurgical microscopes used almost exclusively in the United States are shown in Figs. 1 and 2, special attention being called to what may be called the horizontal-vertical type (Fig. 1), in which a vertical microscope is used for visual work, while a permanently connected horizontal camera is used for photographic work. It is believed that this arrangement presents some decided advantages over the vertical type as well as over the inverted type. I do not believe that these instruments have ever been surpassed by those of German manufacture.

The magnetic holder which I designed many years ago for holding iron and steel specimens has proved, I believe, very serviceable, and is widely used in the United States.

As to the directions in which metallographic investigation should be stimulated as more likely to bring valuable results, I am not one of those who believe that much is to be expected from examination at greatly increased magnifications. Confining my remarks to iron and steel, with the exception of the occurrence of carbon, we are still greatly handicapped by the lack of methods by which other constituents and impurities can be identified and their occurrence studied, and it seems to me that we should endeavour to remedy this condition. Let us briefly consider the various elements or chemical compounds present in industrial iron-carbon alloys.

Carbon.—We have at our command satisfactory means of distinguishing under the microscope the various forms in which carbon occurs in these alloys. I am not of the opinion that carbon may be present, as some believe, in a much greater number of varieties than we are now able to identify, and I do not believe that examination under greatly increased magnification or other methods would advance much further our knowledge of the behaviour of that vital

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element. Carbon is present in iron-carbon alloys either as graphite, or as the carbide Fe_3C, which may be free or which may form with iron a solid solution. I am not attempting at present to distinguish between solid solutions and colloidal solutions or emulsions. I believe that the hardening of steel is due to the retention of the carbide Fe_3C in a solid solution, but I also believe that the solution thus retained by rapid cooling is allotropically different from the solid solution stable above the thermal critical stage.

Phosphorus.—It is believed on good grounds that phosphorus exists as Fe_3P in iron, but unless there is a considerable percentage of carbon present one cannot under the microscope detect the presence of that compound, owing to the fact that it forms with ferrite a solid solution. A method by which steel high in phosphorus could be differentiated under the microscope from one low in phosphorus would be of great service. To be sure, it is believed that segregation of phosphorus may be detected by the Stead's reagent or by similar reagents, but in the light of recent research we are in doubt whether the segregation which we have been in the habit of attributing to the occurrence of phosphorus may not be due in some cases to the presence of some other element or elements; for instance, to the presence of oxygen. Obviously better means of identification are needed.

Sulphur.—We have satisfactory ground for our belief that sulphur in steel unites with some of the manganese present to form particles of manganese sulphide distributed somewhat irregularly in the metal, and that it may also form a sulphide of iron. These can be detected quite readily under the microscope. It is not certain, however, that the dove-coloured inclusions generally assumed to be manganese sulphide contain no other constituents, nor do we know positively that sulphur forms no other compound and that it is not present in any of the other constituents detectable under the microscope.

Manganese.—We believe that some of the manganese present in steel forms, as stated above, manganese sulphide, as well as manganese carbide, and also that some of it is present in solild solution in iron, but with the exception of manganese sulphide it is not possible to detect the presence of manganese in any of its other forms under the microscope.

Silicon.—Silicon is generally supposed to be present as an iron silicide dissolved in iron. It is not possible, however, to verify by the microscope the accuracy of this belief.

Special Elements.—Microscopical evidences of the form in which special elements, such as nickel, chromium, tungsten, vanadium, etc., occur in steel are lacking.

I believe that the discovery of etching or other methods that would permit a more thorough and more exact microscopical analysis of iron and steel and of their inclusions would be of great assistance in the further development of metallography.

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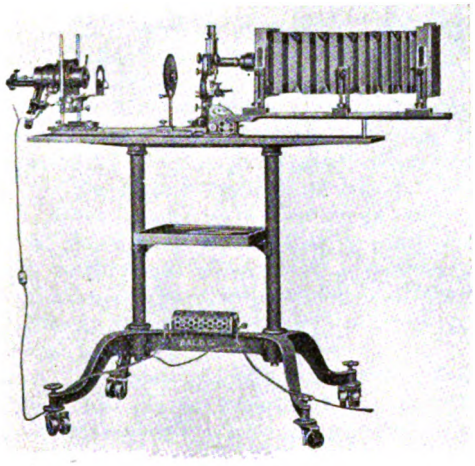

FIG. 1.

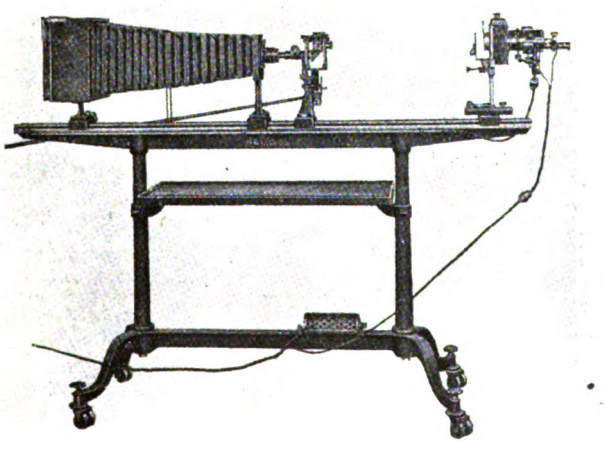

FIG. 2.

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SOME POINTS CONCERNING SHARPNESS IN HIGH MAGNIFICATION MICROGRAPHS.

By Carl Benedicks and Erik Walldow (University of Stockholm)

1. *Microscope and accessories used.*

The following will give a short account of some optical studies executed by us, using the new-constructed metallographical microscope of C. Reichert of Vienna.

The most prominent feature of the new microscope, which is constructed according to the Le Chatelier type, is the very convenient interchangeability of the plain glass illuminator and the prism illuminator. This interchangeability was introduced in consequence of a short paper by one of us,* in which evidence was given of the superiority of the former illuminator at high magnifications. Another innovation is the very convenient adjustment, with index and scale, of the position of the prism—which is of the Le Chatelier type, with two reflecting surfaces—so as to enter more or less, according to the focal length of the objective.

Another detail of the construction is, that the coarse adjustment is operated by a rack and pinion motion of the stage on which the specimen rests (face downwards), whilst the fine focussing is obtained by a micrometer slide motion of the objective and tubes. The advantage is, that a heavy weight on the stage will have no influence on the delicate slide motion.

For photographic work, a green glass filter was used, giving a rather well-defined wave length of 0.5-0.6 μ. Orthochromatic plates (Wellington, anti-screen, backed) were used, and an arc lamp of about 350 c.p., the duration of exposure was increased by this filter in the ratio 10:1. The regular exposure (with filter) was 20 secs. when the glass slide illuminator, 4 secs. when the prism illuminator, was used.

The test specimen was a lamellar pearlite of 0.90 per cent. carbon content, polished in bas-relief on parchment.

2. *Arc lamp and incandescent lamp.*

Fig. 1 gives the specimen at a magnification of 1,200 (arc lamp; immersion apochromatic f = 2 mm., Num. aperture 1.30; projection eye-piece Nr. 2; camera length 65 cm.).

In Fig. 2 a "Half-Watt" incandescent lamp of 60 c.p. was used; of course, several advantages are obtained by a less intense source of light. The exposure had to be prolonged 36 times, to 12 min.

The optical quality of Fig. 2 is still good, but the definition is impaired by a general want of sharpness due to vibration during the long exposure.

It must be pointed out, however, that under quieter conditions photographs were obtained with the incandescent lamp of the very highest sharpness, which in no respect differed from Fig. 1. This proves that the *candle power of the lamp has no influence on the image quality*—a point which, though very natural, scarcely has been proved so far as yet.

* C. Benedicks, *Metallurgie*, Vol. 6, p. 320, 1909.—Dr. W. Rosenhain made some remarks in the same direction in *J. Iron and Steel Inst.*, 1906, II, p. 180 (*see Metallurgie*, Vol. 8, p. 136, 1911).

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The mirror reflecting arrangement provided with the camera proved to be of value, especially at long exposures, as it provides the possibility of a control of the proper focussing during a long exposure, without having any disturbing effect.

3. *Influence of vibrations and its avoidance.*

Even at short exposures with the arc lamp the sensitiveness for vibrations is very undesirable. The whole instrument being very rigidly constructed, the cause of this sensitiveness was by no means obvious. After a detailed examination, it was found that the comparatively great mass of the tube-carrying upright, with the two tubes (ocular and photographic), illuminator and objective, was responsible for the vibration sensitiveness. The remedy was possible to indicate: the objective is to be mounted by itself, on a special upright with little mass, and must have no direct connection with the tubes; if this be the case, then the inevitable vibrations of the tubes will be of no direct influence on the distance between objective and specimen—which is the most sensitive point as regards sharpness. A slight disadvantage introduced by this modification is that the distance between the illuminator and the objective will be subjected to small changes; these, however, seem to be of little consequence in comparison with the considerable increase in insensibility to vibrations which probably will result. Of course, even in works laboratories it is important to be able to produce good high magnification photographs without too much trouble.

In this connection the following may be added.

If the ground of the laboratory is not sufficiently free from disturbance it is necessary to mount the apparatus on some vibration-damping device. Now, it has been found from investigations executed in this laboratory by I. Malmborg* that the simplest thing is to mount the instrument on a solid plate, resting on a thick layer of felt; this, however, must not, as is ordinarily the case, be used in a dry condition, but moistened with a viscous liquid, such as vaseline. The energy of the disturbances is then absorbed through the forced motion of the liquid in the interstices of the felt. This method has been used with great advantage.†

4. *Disposition of diaphragms.*

In the metallographic microscope the cutting off of side-rays by diaphragms is well known for several reasons to be of great importance. As a general principle it can be said that the beam of light is to be reduced as much as possible without interfering with the intensity and uniform distribution of the light, or with the necessary extension of the image.

Fig. 3 gives diagrammatically the illuminating arrangement. In order to work properly, the image of the source of light—as which the opening of the diaphragm B is to be considered—must fall on, or at least near, the illuminator P, and the image of the iris diaphragm I must fall on the surface of the specimen T. The first item, brought about by the lenses L and F, is necessary in order to be able to use the whole of the light power available, and

* *Ann. d. Physik* (4), Vol. 44, p. 337, 1914.
†Benedicks, *J. Iron and Steel Inst.* 1914. I, p. 407 (424).

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to obtain a systematic centering of the light; the second item, effected by lens F and objective O, is necessary in order to limit properly the image on the plate, and to cut off false light so far as possible.

There is, in our view, no reason why the parts of this optical system should be differently arranged (sliding of L) when using a plain glass reflector or a prism reflector; nevertheless, on the microscope examined, as well as on other Continental microscopes, such a difference has been introduced intentionally. As a matter of fact, it was found quite practicable to obtain correct results, so far as the illumination is concerned, with both kind of reflectors, without any variation in the position of L (lens F had to be changed).

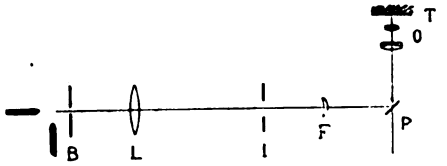

FIG. 3.

5. *Comparison between Le Chatelier prism and* 45° *prism.*

The Le Chatelier prism being so constructed that the lens F is formed in the same piece of glass as the reflecting surface P—which, in fact, is made up of two planes giving successive reflection—it was to be expected that it would produce sensibly better contrasts than a 45° prism with separate lens F, as in this case more reflections must occur.

A careful comparison was carried out. The result was that it was not possible for us to trace any difference in the working of the two kinds of prisms: the 45° prism is practically, so far as contrasts are concerned, not at all inferior to the Le Chatelier prism.

All comparative experiments were so made, by a special projection arrangement, that both prisms (or metal mirror) were exactly in the same position, covering the half of the back lens of the objective.

It was found that for lower magnifications than with the apochromatic f = 2 mm., the Le Chatelier prism has a decided advantage over the 45° prism in so far as it is not necessary, for obtaining a uniform illumination, to cover so much as half of the light area with the Le Chatelier prism as with the 45° prism. Thus at lower magnifications the aperture is better utilised with the Le Chatelier prism. The arrangement mentioned above serves the purpose of easily obtaining for each objective the proper position of the prism.

6. *Influence of the aperture.*

As already remarked, it has been pointed out by Dr. Rosenhain and by one of the present authors that the definition of the image at high magnification is considerably lessened when half of the aperture of the objective is covered by a prism or by an opaque

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mirror, the resolving power being reduced to one-half in the direction at right angles to the mirror edge.*

This fact is amply borne out by our new comparative experiments. Thus, Fig. 4 shows the very best definition to be obtained with a prism illuminator. A comparison with Fig. 1, which was obtained with the plain glass illuminator, gives evidence of the much higher quality of the image obtained in the latter case, thus laying stress on the fundamental condition for obtaining sharp high magnification micrographs: the *full utilisation of the aperture of the objective.*

7. *Comparison between prism and metal mirror.*

It is obvious that with reflecting glass prisms—as well the Le Chatelier as the 45° prism—inner reflections cannot be entirely got rid of. On the other hand, with a metal mirror, such undesirable reflections do not occur, and it is to be expected that the contrasts will improve.

As the result of some direct comparisons, it was actually found that an indisputable, though slight, increase of the contrasts was to be seen on the micrographs obtained with the metal mirror. Thus, a metal mirror illuminator may be of some use whenever particularly strong contrasts are desired.

8. *Influence of the thickness of the plain glass.*

The glass slide provided with the microscope used was 0.45 mm. thick. It may be questioned whether this thickness, on account of the astigmatism introduced, is not too high. On using a very thin glass, 0.10 mm., as a matter of fact, a slight improvement of the sharpness occurred; this, however, was so insignificant that practically the use of the thicker glass must be considered to be quite justified.

If one is at liberty to choose, a thinner glass, of course, should be preferred to a thicker.

9. *Astigmatism introduced by the right angle reflecting prism.*

It seems by no means excluded, that sensible astigmatism could not be introduced by the right angle prism used in the Le Chatelier microscope in order to reflect horizontally the vertical beam of light issuing from the specimen. However, the excellent definition obtained, as in Fig. 1, shows that this undesirable influence of the prism can be entirely neglected. Of course, it is essential that the prism be of a very high optical finish, and carefully adjusted.

10. *Platinised plain glass illuminator.*

As pointed out on an earlier occasion,† it might be possible to increase the light intensity obtained with the plain glass illuminator by using a thin silver or platinum coating. Obviously, the thickness of the metal layer must not exceed a definite value; otherwise a decrease of intensity will result.

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* *See* for instance Dr. Rosenhain's *An Introduction to the Study of Physical Metallurgy*, London, 1914, p. 52.

† C. Benedicks, l.c.

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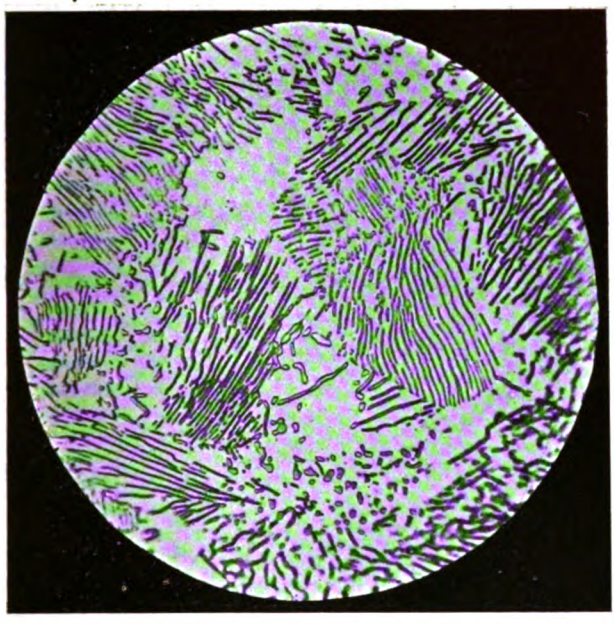

FIG. 1.
Plain glass illuminator, Arc lamp ; 20 secs. × 1200

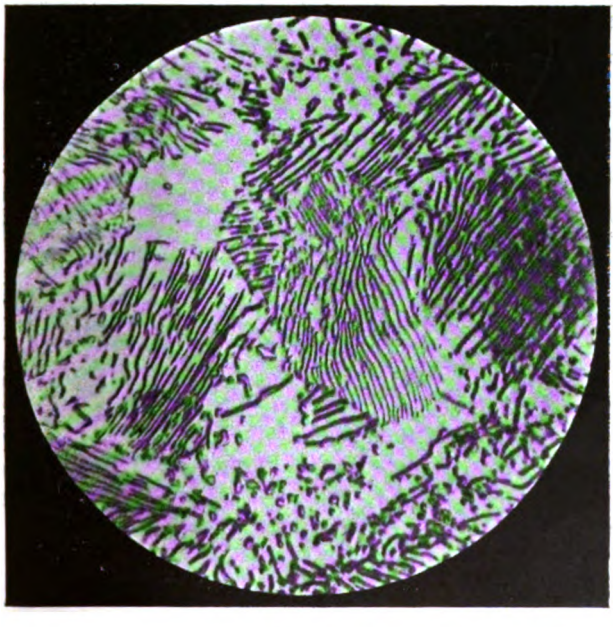

FIG. 2.
Plain glass illuminator, "Half-Watt lamp" ; 12 mins. × 1200.

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FIG. 4.
Le Chatelier prism illuminator, Arc lamp; 4 secs. × 1200

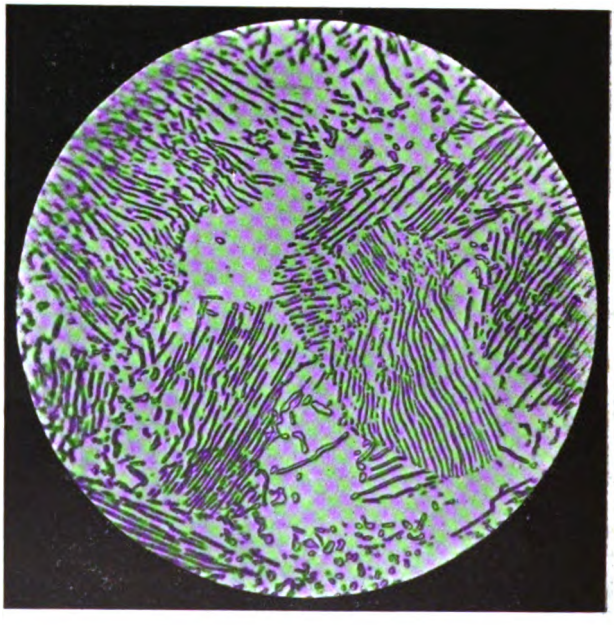

FIG. 5.
Plain glass platinised, Arc lamp; 20 secs. × 1200

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Fig. 5 reproduces a micrograph obtained with a platinum layer of a definite thickness, scarcely providing any appreciable increase in light intensity; exposure 20 secs., as in the other cases. A somewhat thinner coating might have been desirable.

It is of interest to note, however, that the micrographs obtained in this way were characterised by an unusually large extension of the sharp image. The contrasts seem to be somewhat weaker than those obtained with the other illuminators, and possibly this is the reason why on Fig. 5 (in original) are to be seen details, *e.g.*, some characteristic irregularities in the ferrite ground mass, which scarcely are to be seen on any other of the micrographs taken.

Thus it was found from these experiments that any essential gain in light intensity is difficult to obtain by platinum coating, but on the other hand a more detailed investigation is required to find out whether the filtering of the light on passing through the thin metal coating might possibly be of some advantage when it is a question of bringing out a maximum of detail.

11. *Further remarks.*

It has to be added that every exposure was repeated several times, and found consistent with similar experiments, so that, notwithstanding the obvious difficulty of avoiding focussing errors, the results obtained appear to be quite reliable.

A detailed account of these investigations has been published in Swedish in *Bihang till Jernkontorets Annaler*, Vol. 19, p. 537, 1918.

A detailed account will also probably appear in *Zeitschrift fur Wissenschaftliche Mikroskopie.*

Summary.

The investigations were started as a detailed and critical examination of the new Reichert microscope, which is of the Le Chatelier type. It was found to produce excellent results at the very highest magnifications.

Then some points of a more general character were examined, as:

(1) The using of an arc lamp (350 c.p.) or of an incandescent lamp (50 c.p.) gave exactly the same result.

(2) A modification of the microscope is proposed in order to diminish its vibration sensitivity.

(3) The proper arrangement of the diaphragms is discussed.

(4) A Le Chatelier prism and a 45° prism give at high magnification exactly the same result.

(5) A metal mirror gives slightly better contrasts than a prism.

(6) In the plain glass illuminator a thickness of 0.45 mm. does not injure sensibly the image quality.

(7) A slightly platinised glass illuminator gave somewhat finer details than any other illuminator used; this question, however, needs further research.

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AN ORDINARY MICROSCOPE ADAPTED TO METALLOGRAPHY.

By F. Ian G. Rawlins, F.R.M.S.

The purpose of the following brief note is to draw attention to certain details of a more or less minor nature, which, when incorporated into an ordinary microscope stand, render it decidedly efficient for metallographical work, where an elaborate outfit is not desired. Although post-war models are now appearing by the leading makers for this branch of microscopy, there is a decided advantage in being able to use an ordinary stand, and the expense involved in the modifications is very moderate. Lastly, the additions are such that they can be easily carried out, even in the present abnormal state of the trade; and they are no detriment to work on transparent objects.

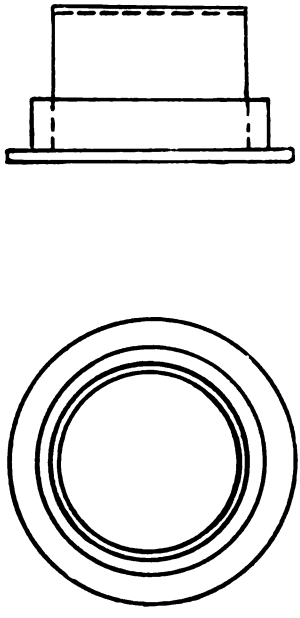

FIG. 1.

Vertical and Horizontal Sections of Plug.

(1) *Substage Fitting.*

The point of this is to overcome the trouble inherent in the use of ordinary stands for opaque objects with the vertical illuminator, *i.e.*, that on re-focussing, the centering of the illuminator and light-source is disturbed. Assuming that the stand possesses no substage apparatus (apart from the mirror), a focussing substage is fitted, provided with coarse adjustment, rack and pinion. Instead of the usual condenser, a solid brass plug (circular, and of the shape

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sketched in vertical section,) is inserted into the ring. The top is provided with a slightly bevelled edge, into which fits a glass slip on which the plasticine holding the specimen is placed as usual. This can then be focussed upwards and downwards, avoiding any movement of the body-tube. To substitute another specimen, all that is needed is to rack down, swing the fitting out of the optic axis, take out the plug, insert another levelled specimen as already described, re-insert the plug, and focus as before. Of course, if only objectives are being changed, the focus can be re-set at once. An adapter fitted to the body-tube may be wanted if the rackwork on the stand is limited. The central aperture in the stage is generally too small, and should be enlarged for these additions. In the event of transparent work with condenser, polariser, etc., being contemplated, the focussing substage is ready at hand, the appropriate fitting being substituted for the afore-mentioned plug.

(2) *Objectives.*

Mounting in short barrels is very desirable for use with the vertical illuminator. There is often considerable difficulty in obtaining objectives so arranged from the makers. The following alteration, easily carried out, may assist. The lower part of the barrel is

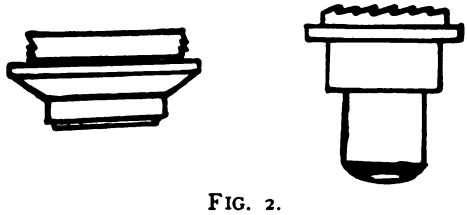

FIG. 2.

Carrier and Unscrewed Part of Objective.

unscrewed, and then inserted into a carrier bodily, which latter is provided with a standard thread, attaching to the vertical illuminator, and bringing the back lens of the objective very close to the reflector. Two lenses so treated, a $\frac{1}{3}$ inch and a $\frac{1}{6}$ inch, in the writer's possession give excellent results in practice.

(3) *Illumination.*

A type of " Half-Watt " lamp made in Holland has been found admirable. The 200 candle-power size is amply sufficient. By noting that the ring-filament in these lamps gives a very solid and concentrated area of light, and using a bull's-eye condenser of small aperture, it is possible to get effects closely resembling a " point-source " of light. The very moderate cost of these lamps compared with, say, a " Pointolite," is greatly in their favour, and they are quite powerful enough for magnifications up to 600 diameters in metallography.

In conclusion, apart from general ideas, the author disclaims any question of having originated the above improvements. His thanks are due to Messrs. H. F. Angus and Co. for their skilled assistance.

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THE MICROSCOPE IN METALLURGICAL RESEARCH.

By E. F. Law.

It would be difficult to over-estimate the importance of the part played by the microscope in metallurgical research during the last 15 years. Its introduction threw a flood of light on problems hitherto unsolved, and it was not surprising that the early work of the pioneers—Sorby, Osmond, Roberts-Austen and others—was followed by a rush of eager recruits anxious to take part in the campaign. Nor was it surprising that this display of zeal should be followed by a lull, if not an actual reaction; such periods invariably follow a period of exceptionally rapid progress, and when they occur it is wise to take stock of the existing position and endeavour to prepare the way for the next advance. With that object in view we may briefly consider the metallurgical problems which have already been solved by means of the microscope, and then turn to some of those which are awaiting solution and which require either more knowledge or more perfect instruments.

Problems Solved.—Before the introduction of the microscope we knew from the chemical analysis of an alloy its ultimate chemical components, but we did not know in what form those components occurred. Probably the only exception to this rule was to be found in the case of carbon in cast iron, which was invariably divided into free or graphitic carbon and combined carbon. The microscope altered all this, and explained not only the relationship between the structure of the alloy and its mechanical properties, but the structural alterations and consequent changes in mechanical properties produced by heat treatment.

Problems to be Solved.—With very few exceptions, it may be said that the finer or smaller the structure of an alloy, the more useful it is from a commercial standpoint; and it frequently happens that the best of our commercial steels possess so fine a structure that they are imperfectly resolved by the highest powers of the microscope now available. How often do we read in descriptions of microstructures such expressions as "a confused groundmass" or "a matrix whose structure is not resolved by the microscope"? Another problem awaiting solution is to be found in the intercrystalline weakness of metal. During the last few years a wonderful edifice of hypotheses has been erected on the foundation of a so-called amorphous phase which is said to exist between the crystals of a metal, and this amorphous material is made to serve as an explanation either of its strength or weakness.

Unfortunately, there is very little direct evidence in support of these theories; but with a higher degree of magnification it is possible we may learn more of the intercrystalline structure of metals. Even of the crystalline structure we know very little, and there is scope for much research on the "dendritic" structure which is shown on heat-tinting, and which has been so beautifully developed by Humfrey.

For these and other investigations we require instruments which will give us a higher degree of magnification, and we look to the manufacturers for their assistance. But, if we are provided with such instruments, we, on our part, must be prepared to supply a much higher degree of skill in the preparation of samples for examination than is commonly met with.

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DEVELOPMENT OF THE METALLURGICAL MICROSCOPE AND ITS SUGGESTED APPLICATION TO SOME UNSOLVED PROBLEMS.

By HERMAN A. HOLZ, NEW YORK.

Every step forward in the development of apparatus for metallurgical research work is followed by an increase of our knowledge of the particular field of metallurgy for which the instrument serves. In other words, suitable apparatus have to be developed to a high stage of perfection before we can make accurate and reliable determinations which enable us to gain valuable knowledge of certain facts which were unknown to us before or about which we were not quite certain.

The development of the thermo-electric pyrometer by Le Chatelier enabled us to find the transformation regions in steel, Sir William Roberts-Austen's apparatus—making use of thermo-electric forces—permitted us to determine these transformation regions with great accuracy and in a convenient manner, resulting in systematic research work which forms the basis of the art of heat-treating steel.

The most important apparatus which enable the metallographist to find the way towards improvements in the structural details of steel and to control the correct thermal treatment to which he subjects the material, are the microscope and the permeameter. The microstructure of steel can be observed and photographed by means of the microscope, while it can be measured and expressed in definite figures by means of the permeameter, thus permitting quantitative determinations. The success gained in recent years in obtaining higher efficiency from definite alloys, especially alloy steels, and in developing steels and bronzes of greater strength, has been due to systematic metallographic, especially microscopic, research work.

As the methods of microscopic investigation have been improved by the development of more efficient etching processes, so have the design and construction of metallurgical microscopes been gradually developed to a high stage, in regard to the quality of lenses, source of light, vertical illuminators, etc., as well as to rigidity and usefulness of mechanical arrangements. While the pioneer work on the microstructure of metals was carried on by means of ordinary (bacteriological) microscope stands, it was soon found that the investigation of opaque substances, without using cover glasses over the object, necessitated changes in the illuminating system and in the grinding and mounting of the objectives. The vertical illuminators now largely used for this purpose were developed in England (45 degree plane glass reflector by Beck) and France (prism reflector by Le Chatelier, first made by Pellin and Nachet). The objectives used in connection with these illuminators have to be mounted as short as possible; the nearer the reflecting surface stands

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to the objective, the more even is the illumination obtained. In the method of plane glass reflection, the rays of illumination and of the image penetrate the entire objective simultaneously; the final image suffers somewhat thereby, and does not appear as sharp as with the prism illuminator. This disadvantage can be remedied somewhat by decreasing the opening angle of the objective. The important advantage of the 45 degree plane glass illumination is that the light strikes the etched surface at exactly 90 degrees, so that with the highest magnifications and in working with very fine, slightly etched specimens images richer in detail and free from spectral colours are obtained; the rays of light are, in this case, uniformly distributed over the entire field covered by the objective. In applying the Le Chatelier prism illuminator, one half of the objective serves for illuminating the specimen, the other half for producing the image. This arrangement offers the advantage that by dividing the function of the objective the formation of reflexes is reduced and the full angle of opening of the objective is utilised. The images thus obtained are clearer and sharper, of special advantage in photography. On the other hand, fine details of structure may be lost through the one-sided illumination striking the etched surface at an angle. Since both forms of vertical illuminators possess certain distinct advantages and disadvantages, it will be found very convenient to be able to change quickly from one to the other, and to select the one which will give the more satisfactory image, depending upon the nature of the microstructure under investigation and upon those points that the metallographer desires to bring out more prominently in his micrographs. The latest metallographic outfit brought on the American market by my firm possesses this important feature of " selective " vertical illumination.

Many of the steel works' metallographers prefer now the inverted form of microscope, first designed by Le Chatelier and first made by Pellin. I desire to mention here that the original Le Chatelier-Pellin outfit carried a stage supported on one point only, which was easily bent out of focus, and did not possess sufficient rigidity. Le Chatelier designed in 1911 another and very much improved inverted stand, also made by Pellin, which carries a firmly supported stage and which was imitated by German and Austrian manufacturers. Nevertheless, the largest number of German steel works, amongst them the Krupp works, preferred the new Le Chatelier-Pellin stand which was marketed in 1912 and 1913 with much success in Germany by Dujardin, who imported the microscopes from Paris and fitted them with Zeiss apochromatic objectives, thus combining best mechanical design with good optical equipment.

Returning to the question of metallurgical microscope stand design, I want to say that the popular form of inverted stand really has only the one advantage of eliminating the necessity of levelling the specimen, and this advantage disappears mostly in using an oil immersion lens. The disadvantages of the inverted stand are the limited field which can be observed, the large leverage of the stage resulting in magnification of vibrations, and the impossibility of working with daylight. Microscope stands have been successfully designed (Félix Robin's outfit, formerly made by Collot, Paris), which combine the advantage of horizontal camera with firmly sup-

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ported stage below the objective, thus permitting the convenient investigation and photography of heavy specimens, observation of their edges, use of daylight, and large reduction of vibrations. While these outfits are not available any longer, it seems to me that the development of satisfactory photomicrographic apparatus for metallography should follow this general design, and not the inverted design, which possesses several disadvantages more important than its one single advantage.

Amongst other microscopic problems awaiting further development, besides higher magnification, are: the utilisation of polarised light for metallographic investigations and the application of kinematographic work to the study of structural changes in metal sections exposed to mechanical stresses or varying temperatures. The pioneer work in solving the apparatus development problems for these studies has been successfully carried out, and the high value of such investigations will be appreciated. It is to be hoped that research workers will take up systematically this work, which has been successfully started. Further microscope development, offering no more difficulties, will be in the direction of stereoscopy. We are born with two eyes, and used to see with both of them; mon-objective binocular microscopes, for work with the highest magnifications, have been successfully developed, and there seems to be no reason why this instrument development should not be applied to advantage to metallographic practice. I believe that the near future will see a large extension in the use of binocular optical instruments.

I would not like to omit here to mention some important progress made in Great Britain in the development of metallographic equipment: The Edison-Swan " Pointolite " (tungsten arc) lamp, which is the ideal source of light for photomicrographic work, and the Wratten and Wainwright light filters and special plates for photomicrography. These products represent the best that has ever been developed in their respective lines, and every metallographer will find the use of these appliances extremely valuable in his work.

In ending my contribution, I want to make a few additional remarks about the importance of " magnetic analysis " in metallographic research and routine work. The use of higher magnifications in microscopic investigation will most probably lead to valuable results, although we must always remember that the higher we magnify the less we see, *i.e.*, the field of observation is getting smaller with the use of objectives of higher powers. Magnetic analysis (the accurate determination of the various magnetic properties of iron and steel by means of a standard permeameter) enables us to draw distinctions between steels where the present methods (microscopic, hardness, tensile tests) fail to make differentiation. Microscopic investigation of steel gives results which are qualitative, rarely quantitative. The preparation of micro-sections often releases stresses in the metal to be studied, and, in general, tests of this kind require a great deal of individual judgment and experience. Magnetic data permit quantitative measurements of the state of micro-structure and the interpretation of test data leaves no room for conjecture.

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Such magnetic investigations can be carried out successfully only by means of a perfectly reliable permeameter and only by determination of *all* the magnetic characteristics of the material under investigation. Permeameter equipment has been recently developed to a high stage of perfection, combining simplicity of operation with perfect accuracy of measurements (Fahy Simplex Permeameter), and since then the application of magnetic analysis to metallographic investigations has made rapid progress in the United States. It is to be hoped that British metallurgists will apply this excellent method to the solution of their problems, and will co-operate with American research workers, to considerable mutual benefit.

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General Discussion.

In inviting **Dr. W. H. Hatfield** to offer some remarks on the metallographical side of microscopy, the Chairman suggested that in view of the short time available for general discussion of the many important papers presented on this subject, the discussion be continued at Sheffield, and, if possible, also at Glasgow.

Dr. W. H. Hatfield: I should like to say that I know I should be expressing the general feeling of the Council of the Metallurgical Society at Sheffield in saying that we have great pleasure in accepting your invitation. If you will let us have copies of these papers, particularly the metallurgical section of them, we will have them thoroughly discussed, and, if you desire it, we will send Mr. Spiers a copy of the discussion.

Speaking on the papers, I think one can safely say that we have in Sheffield many large firms who have well equipped laboratories where these different types of microscopes are in use every day. I should like to congratulate the President on the interesting paper by Mr. Elliot and himself. I think that the work contained in this paper typically represents what we are able to do with the microscope in our study of steel. We (Brown-Firth Research Laboratory) have some photomicrographs upstairs; they are really on the same lines as those of Sir Robert Hadfield, but we have gone as far as 8,000 magnifications. I think Sir Robert will probably agree with me when I say that 1,000 diameters really represents the limit of adequate resolution which we are able to obtain in our general practice, and that if we go in for these higher so-called magnifications—I refer both to his illustrations and to ours—we are getting enlarged pictures, but we do not obtain really much more information as to the structure of our materials, and from that point of view it is interesting to refer to the paper on Dr. Sorby which the President has put before us. I notice there that Sorby made great advance in the 'eighties because he was able to use sufficiently high magnification to see the structure of the pearlite. Every time that we have been able to get a still higher resolution we have obtained more fundamental knowledge with regard to steel, and whilst I feel that 1,000 is at present our practical limitation, I am certain that if only you experts in the construction of the microscope can go still further, we shall obtain still more fundamental information. For instance, I remember studying what we know as black steel at 250 to 500 diameters, but we got inconclusive information, but as soon as we got to 1,000 diameters we had definite information and a complete solution of our difficulty. There are two problems which I would like to point out to you microscopists, or rather to the makers of microscopes, which are awaiting solution. One Dr. Aitchison deals with very ably in his paper, *i.e.*, notched bar brittleness. I

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will not go into it except to say that there are two fundamentally different conditions of the same steel, which at present we are not able to obtain the reason for by means of the microscope, and I think we have a right to feel that we should. I do not hesitate to make a confession to you. An artilleryman does not worry unduly as to how the gun was made or who made it. I represent exactly that type of scientific investigator who uses a microscope, and, like the artilleryman, I am telling you what we would like to do with the gun. Therefore, I think it is up to the makers of the microscope to help Sir Robert Hadfield and many people like myself who are engaged in these investigations, out of our difficulties. In conclusion, I would tell you that all metallurgists, whether they be working on steel or non-ferrous metals—brass, copper, gold—are faced with the difficulty of obtaining an adequate solution as to the cause of the effect of cold work on metals. We discuss the amorphous theory; many of us believe in it; we ought to be able, by means of the microscope, if you will give us a suitable tool, to obtain an adequate solution of that problem. Why has cold work the great effect it has in hardening metals? Gentlemen, I consider the solution of that problem is awaiting the excellence of your products.

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The following contributions have been received to the discussion on the paper by Sir Robert Hadfield and Mr. T. G. Elliot.

Mr. A. T. Adam and Mr. F. S. Merrils: In studying the microstructure of steel wires we have found it necessary to employ high magnification. The difficulty in resolving the structure of carbon steel wires is due in the first place to the nature of the chief constituent in properly heat-treated wire, viz., " Sorbite," or " Sorbitic pearlite," and secondly to the minuteness of the structure caused by cold work.

Some time ago we were fortunate in securing a very good Leitz 1/12 in. oil-immersion achromatic objective, N.A. 1.3, which has enabled us to obtain sharp photographs of wire up to a magnification of 2,500 diameters. This we have found to be about the highest magnification at which good definition and detail are retained with this objective. In certain special cases we have gone up to about 5,000 diameters with distinct advantage.

One of the contributors, being engaged in an investigation on " The Relation of Heat Treatment to Cold Work," has found these photographs of great service in illustrating the effect of cold work on the structure, and hopes to have them published in the Carnegie Scholarship Memoirs of the Iron and Steel Institute this year.

It is admitted that there is a certain loss of detail in these photographs as compared with visual examination, but this detail is lost in any photograph where an ordinary eye-piece is used. On the other hand, certain features which are barely visible in a photograph at, say, 1,500 diameters, are more pronounced in the enlargement obtained by increased camera length.

In view of these attempts at high power photomicrography, we are therefore extremely interested in the authors' work in this direction, and we are in entire agreement with them in the belief that there is a great field for further exploration in this direction.

One or two examples of photomicrographs at high magnification are given below with details. The source of illumination used is a tungsten arc 500 candle-power " Pointolite," made by the Edison Swan Electric Co., Ltd. With this source of light it is only necessary to use a single condenser to focus the image of the incandescent arc on to the plain glass illuminator. It may be of interest to add that Wratten and Wainwright colour filters, M series, were used with Wratten M Panchromatic Plates in taking these photographs.

Fig. 1 shows that it is possible to obtain good definition in a photograph at this magnification. The subject is possibly not one that requires high magnification in itself, but it is useful for purposes of comparison with subjects that do require such magnifications, *e.g.*, Fig. 3.

Apart from this, it appears to show that " pearlite " is a more complex constituent than lower power photographs indicate. The contributors have always considered the idea that " pearlite " is constructed of alternate layers of ferrite and iron carbide completely

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separated, to be rather vague. This photograph suggests that complete separation has not taken place in the laminated form, and occurs only in the spheroidised form; *e.g.*, Fig. 2.

The appearance of sub-laminations in Fig. 1 is not a false effect due to excessive cutting down of the iris diaphragm, as no diaphragm was used in this instance. A slightly false effect, due to this cause, is evident in Fig. 5, which was taken expressly for this contribution.

Fig. 3 shows a subject in which the laminations are too fine to be clearly photographed at a magnification of 1,500 diameters. The photograph demonstrates that even air cooling a rod about $\frac{1}{4}$ in. diameter is not sufficiently rapid to arrest the partial production of "pearlite." It will be noticed that the constituent which we have called "sorbitic pearlite" is partly cellular.

The difference between these structures is not apparent at lower powers.

Fig. 4 is to be compared with Fig. 5. In spite of the slightly false effect in the latter, caused by the iris diaphragm, it draws attention to the existence of a feature which might easily escape notice, but which is apparent on closer examination, in Fig. 4, namely, the sub-laminations.

Mr. Henry M. Sayers: These photomicrographs of steel at 5,000 and 8,000 diameters are very fine, and testify to the skill and patience of the authors. They confirm the accepted theory that no new details can be revealed by magnifications incommensurate with the N.A. of the objective. With an N.A. of 1.4, 1,000 diameters shows all that can be seen, but, of course, greater amplification may be useful for diagrams to be displayed to large numbers of people, at once, just as lantern slides are magnified by projection.

The authors state that the illuminant used was a 20 ampere alternating current arc, the arc being focussed on the stop or aperture of the vertical illuminator. Presumably one or other of the carbons was so focussed. This adds to the merit of the work, for certainly an A.C. arc is less satisfactory in intensity and form of the radiant than a C.C. arc crater.

It will probably be found that one of the larger tungsten arc lamps is better than an A.C. arc. It is true that the tungsten arc requires continuous current, but this can be got from an A.C. supply with a simple form of auto-transformer and rectifier. A nominal 100 c.p. Pointolite, taking about $1\frac{1}{4}$ amperes, gives satisfactory negatives of steel with 5 minutes' exposure, at 1,200 diameters, using a light filter denominated "5 times," and Wellington "Anti-Screen" plates.

The Pointolite lamp is somewhat more convenient for the necessary source emplifying lens system than an arc. The exposures above mentioned were taken with a combination which magnified the source about three diameters, giving a field of 3 in. diameter, *i.e.*, comfortably filling a quarter plate. With no amplifier the field on the plate was only about 1 in. diameter. Greater amplification can be obtained if required by varying the lens distance of the combination.

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FIG. 1.

1.2 per cent. Carbon Steel, annealed. Magnification 5,000 diams. approx. K.1 Colour Filter.

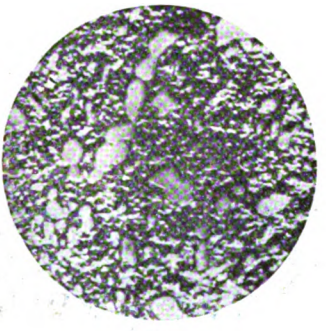

FIG. 2.

1.2 per cent. Carbon Steel Wire. Re-heated at 650° C., showing Spheroidised Cementite. Magnification 4,000 diams. approx. Red Colour Filter A, showing maximum detail.

FIG. 3.

900° C., showing Sorbitic Pearlite. Magnification 3,000 diams. Orange 0.85 per cent. Carbon Swedish Steel. No. 5 S.W.G. Rod. Air-cooled from Colour Filter G.

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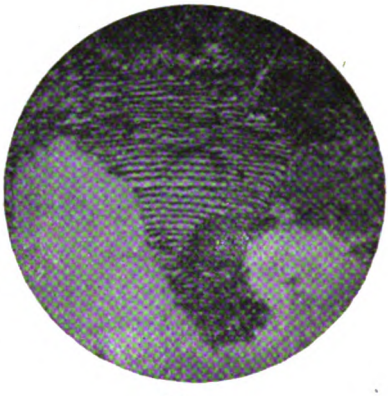

FIG. 4.

0.5 per cent. Carbon Steel Bar, annealed. Magnification 1,500 diams. Red Colour Filter A.

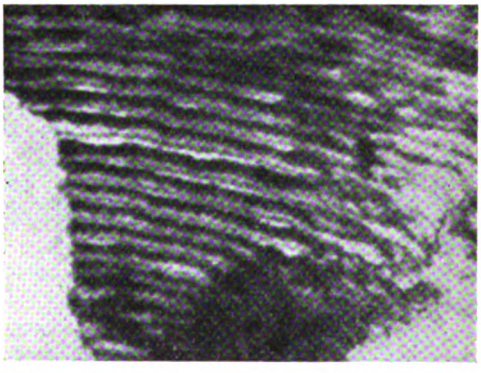

FIG. 5.

Portion of same field. Magnification 4,500 diams. K.1 Colour Filter.

NOTE.—These reproductions have been reduced by one-third from the original photographs.

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Professor H. M. Howe (*communicated*).

All our present conceptions of the nature of alloys are due to the microscope. The labours of Sorby, of Osmond, and of Le Chatelier, brought us to the point at which we recongise pearlite as an eutectoid, the great turning point in the progress of our conceptions.

One finds important problems solved quickly and surely by means of a magnification of 2,000 which completely baffled us when our magnification was confined to 200 diameters. Thus, just as the first step of slight magnification opened up a new world to us, so a second step has brought new and important conceptions of great potential service.

Have we not good reason to hope from the past that like important knowledge awaits further increase in our powers of magnification? Have we not every reason to believe that this knowledge is there to-day, behind that closed door, awaiting its unlocking by him who shall devise the key? No doubt the technical difficulties are extreme, but surely the reward which awaits success should be proportionally great.

A group of papers, presented and taken as read, discussed various other aspects of the microscope, its use and applications.

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THE MEASUREMENT OF GRAIN SIZE.

By Zay Jeffries, Cleveland, Ohio.

Just as the telescope has given us certain information in astronomy which we know no other way of obtaining, so the microscope has permitted us to obtain direct knowledge concerning many things unresolvable with the naked eye. Much of the knowledge gained with microscopes would not be obtainable in any other way. For example, the quantitative determination of grain size of fine grained metal is only possible because of the microscope. The purpose of this brief note is to point out a case in which chemical analysis varies but little, and success or failure depends on the grain size which can be determined only with a microscope.

In the mechanical working of tungsten it was found that some lots of metal would work well, and some only with great difficulty. Sometimes the metal would be so hard that it could not be drawn to the smaller sizes; it would either break too frequently or the die wear would be so great that it could not be tolerated. A careful study of these materials was made from both chemical and physical standpoints. The chemical analysis was found to be so nearly constant that errors of analysis would mask any differences which might actually be present. It is not maintained that slight differences in analysis did not exist, but only that the determination of the impurities which, aside from thoria, probably did not exceed 0.05%, gave no definite clue to the difficulty.

It was found that the variation in grain size was greater than the variation of any of the chemical or physical properties, and that the working properties varied with the grain size. The larger grains had more ability to stand extreme deformation than the smaller ones. On the other hand the tendency to break in the early stages of working was greater in the coarse grained material. If the grains were too small in the tungsten metal containing 0.75 per cent. ThO_2 the wires broke frequently in the smaller sizes and the die wear was excessive. In this metal the danger line is reached if the number of grains per square millimetre exceeds about 6,000. On the other hand, it is desirable that the tungsten metal have an inherent high resistance to grain growth to insure a long life in the lamps. This factor is usually satisfied if the number of grains per square millimetre exceeds 1,500. It is, therefore, desirable to control the grain size between 1,500 and 6,000 grains per square millimetre in the ingot.

In the early days of working tungsten no such control was exercised and lots of metal were encountered which were unworkable, and no one knew the reason. The inference now is that the ingots were too fine grained since it is possible to reproduce these results with fine grained metal to-day. A contributing, and sometimes the major cause of trouble was the failure to eliminate the oxide of tungsten, but even this is more readily detectable with the microscope than by chemical analysis.

Every lot of tungsten metal made at the Cleveland Wire Division of the General Electric Company is now tested for grain size; in fact, treated to give the proper grain size in many cases. The lots not falling

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within the proper limits of grain size are not subjected to the working process, which costs on the order of twenty times as much as the preparation of the ingot.

The method of quantitatively determining the grain size has been described by the author in the *Transactions of the Faraday Society*.* A circle 79.8 millimetres diameter is drawn on a ground glass, and the image of the properly etched sample is brought into good focus. The grains intersected by the circumference of the circle are counted and multiplied by .5 (in the paper above mentioned this factor was given as .6, but later results show that .5 is both more accurate and simpler to use),† and this product is added to the number of grains completely included. The sum is the number of whole grains within the area represented by the circle.

It is true that the determination of grain size in other metals, such as alpha brass, has been used as a help to works control, but the application of this is not very extensive and not as necessary as with tungsten. Other differences are manifest which may be easier to determine than the grain size. Several metallographists have told the writer that they had investigated the variations in grain size and found that the physical properties did not vary greatly with considerable variations in grain size, and hence they had concluded that the test was not suitable for their purposes. It is for this very reason that the writer believes that many other special cases will arise in which a considerable change in grain size will correspond to but slight differences in certain other properties (like the working properties in tungsten), and these properties may be controlled within narrow limits by controlling grain size. In fact, metals or alloys other than tungsten have certain properties which can be controlled only by controlling grain size or other structural features, but these structures are produced by uniform processing determined by experience, and the actual quantitative determination of grain size is not necessary. With the modern demand for uniformity of product and high standards, the manufacturing tolerances will be reduced, and extended use of grain size control may be expected. Even now the defective loss in the mechanical working of metal could be reduced in many instances by properly controlling the grain size in the various stages of processing. In large plants the lessening of the defective loss a fraction of one per cent. would more than pay the cost of investigation and upkeep of these control methods.

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* Vol. XII, Part I, 1917, p. 40.

† Metallurgical & Chemical Engineering, p. 185, Feb. 15, 1918. Also Sano and Ohashi, Proc. of the Physico-Mathematical Society of Japan, 3rd Series, Vol. I, No. 7, p. 216, treat this method of grain size determination mathematically, and conclude that "Jeffries' formula . . . is quite sufficient for practical purposes."

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NOTE ON MICROSCOPE MICROMETRY.

By Professor W. M. Thornton, D.Sc.

In the increasing use of the microscope by engineers for the measurement of small objects which cannot be dealt with by usual micrometric methods, the need is occasionally felt of a means of calibrating the eye-piece micrometer. For this purpose it is convenient to have a scale one centimetre long photographed on a glass slide, and divided into millimetres, half millimetres, tenths, hundredths, and possibly thousandths.

This is covered with a thin slip of mica or glass cemented on round the edges.

The object of this note is to call attention to the convenience of the combination of such a scale with a fully divided ocular micrometer as a means of calibrating rapidly and with sufficient accuracy for most purposes, any system of eye-piece and object at any extension, in microscopes not fitted with travelling micrometer stages. The idea is no doubt old, but enquiry over a wide area has shown that it is not in use by those making daily observations, and to engineers and physicists who are not in immediate touch with microscope theory and formulae it may be useful to have both a loose scale in the eye-piece and a graduated slide for calibration.

Dr. Maurice Langeron, Chief of the Laboratory at the Medical Faculty, Paris, presented the following papers on behalf of **Dr R. Bazin.**

MAKING ENLARGED-SCALE DRAWINGS AFTER BAZIN.

The device dispenses with a camera lucida, and consists of an ordinary biconvex lens A, giving a virtual, erect and enlarged image of the object OO, which is placed between the lens and its focus; Fig. 1 explains the arrangement. An image of the paper and of the point of the pencil C is formed on the plane on which the object rests, being produced by the plano-convex lens B of short focus; this image is real, reversed and reduced in size, because the paper is at great distance beyond the focus. The biconvex lens A enlarges both the small image of the pencil point and the object itself, which are in the same plane. In drawing one has merely to trace the outline of the image.

EYE-PIECE GRATICULE FOR DRAWING, MEASURING AND COUNTING.

(*Bazin's Réseau Oculaire.*)

When painters wish to copy a picture on a different scale, they divide the photograph of the picture, as well as the canvas on which they are going to paint, into small squares. Each little square is then filled up.

The réseau oculaire, or eye-piece graticule, consists of a plate on which lines, very fine, yet as distinct as possible, form a system of squares of 1 mm. size. This plate is placed on the diaphragm of the eye-piece.

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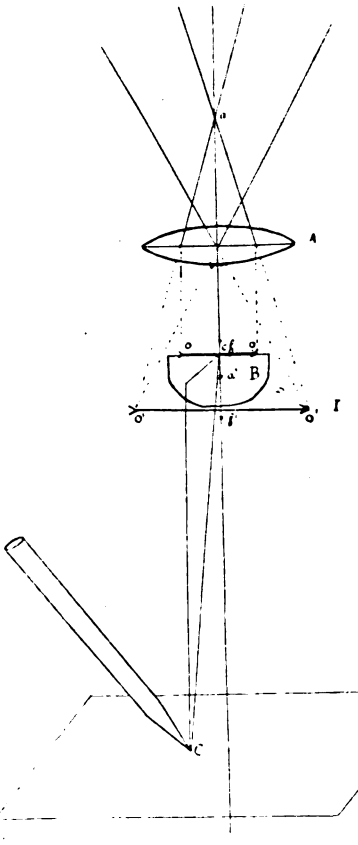
In drawing one makes use of squared paper, and the microscopic image is reproduced in the way that the painter copies his picture. To facilitate taking measurements, one of the squares in the centre (see Fig. 2) is subdivided into four smaller squares, and one of the small squares is again subdivided in the same way, with the aid of a micrometer objective. Thus measurements can easily be made.



A. Biconvex lens
B. Plano-convex lens of short focus and o.o erect and enlarged
I. Vertical Image
O.O. Object
aa Focus of A
ff Focus of B
C. Pencil Point
c. Image of Pencil Point

FIG. 1.

When particles are to be counted, the diluted blood or bacteria preparation is placed in some cell which need not be squared; the thickness of the cell must be known. It will be possible to count the number of globules approximately, provided that one can get them displayed in a single layer. The volume of the little drop adhering to the pipette being known, the area which the drop occupies can be measured with the aid of the graticule; by counting the mean number of red corpuscles per square, an approximate estimate

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can further be formed of the number of elements containd in the drop. In the same way parasitic organisms and leucocytes can be counted.

The réseau also serves as a reference system of co-ordinates, and can replace the pointer of the eye-piece. (The device was described in the *Bulletin de la Société de Pathologie Exotique*, Vol. XII., p. 135, 1919.)

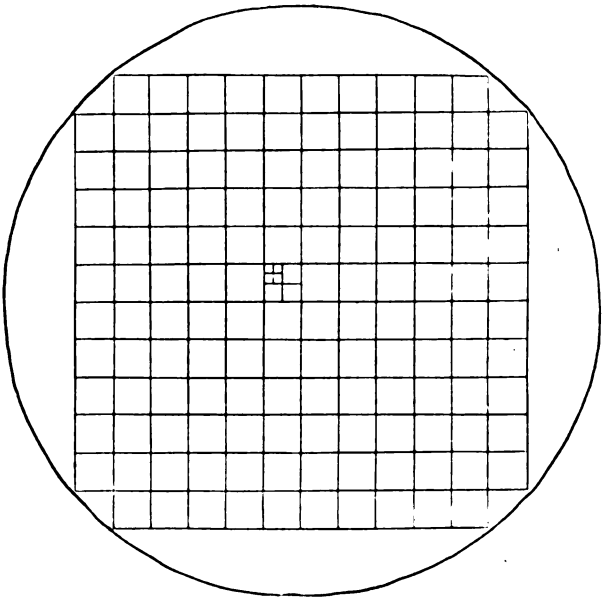

FIG. 2.

BAZIN'S CAPILLARY CHORESIMETER.

The haematocrite makes use of centrifugal force for the purpose of counting the number of blood globules. With a similar apparatus bacteria suspended in distilled water can be counted; their small size calls for a special device, however.

A glass flask, of a capacity of 20 cub. cm., is terminated by a capillary tube, 0.2 mm. bore, 4 cm. long. The extremity of the tube is closed by a rubber disc kept in position by a stirrup which can be turned about its axis (see Fig. 3). The stirrup is supported by a metal collar encircling the neck of the flask. The upper aperture of the flask is hermetically closed by a metal stopper, which is provided with a rubber packing and screwed into the collar. To prevent any slipping of the stirrup during the centrifugation, the capillary tube, together with the stirrup, is enclosed in a sleeve of copper or brass. The capillary tube is filled with distilled water, the rubber disc is applied to its lower end, and the stirrup turned down. The bacteria suspension is poured into the flask, the stopper screwed in, and the sleeve mounted. The apparatus is then placed in the container of the centrifugal machine, which is turned for ten minutes at 7,000 revolutions. The bacteria collect in the capillary

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tube, and are watched through the two symmetrical slots in the sleeve. Measurements are taken with the aid of a vernier and a lens. The apparatus is calibrated with the aid of bacteria suspensions of known numbers.

The capillary tube should neither be too fine nor too coarse; in the former case the capillary might become clogged, in the latter the precision of the measurement would be impaired. The dilution

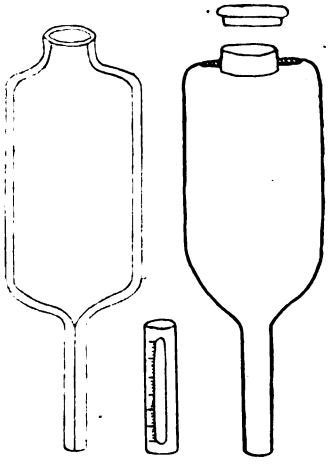

FIG. 3.

of the suspension must also be suitable, as a concentrated preparation would entirely fill the capillary. The distilled water used should carefully be filtered, since a small particle, *e.g.*, of cotton, would stop the tube. In order to facilitate comparative determinations, a standard tube containing a suspension of known titre, of particles of known dimensions and density, should be used; porphyrised kaolin may serve for this purpose, after levigation and filtration.

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THE GRAYSON RULINGS

By Dr. A. E. H. Tutton, F.R.S.

It must have been with the deepest regret that workers with the microscope heard of the premature demise of Prof. H. J. Grayson, of Melbourne, the remarkably gifted maker of the well-known "Grayson Rulings." Those who have used the rulings have been struck with both their accuracy as regards spacing, and the extraordinary sharpness of each individual line, especially in the case of those on speculum metal. The truly wonderful guiding of the diamond point by the late Prof. Grayson's own unique master hand, no less than the perfect construction of his ruling machine, which enabled such accurate spacing to be obtained, have never ceased to impress those who have worked with these rulings. Their merit begins at the point where the other rulings so well known to us, such as those of Rowland and of Michelson, leave the field, namely, above 20,000 to the inch. His extreme rulings of 120,000 to the inch, are a direct challenge to the microscope, for they represent its highest resolving power. While these wonderful rulings, and those only a degree less impressive of 100,000 and 80,000 to the inch, are of great use to us in studying high resolution, with natural microscopic objects presenting detail of great minuteness, and also in actual calibration and measurement of the detail of objects of such extreme minuteness, it is probably with the more moderately spaced rulings of 60,000 and 40,000 to the inch that the most important work is to be done.

The writer has already called attention, in his memoir* to the Royal Society on the Interference Comparator for Standards of Length, to the fact that the Grayson rulings of 40,000 to the inch spacing are capable of becoming of great importance in metrology, as fiducial marks, the middle one of five such rulings forming an excellent signal-mark. For, as was pointed out in the memoir, the 40,000th of an inch is the wave-length of red light, very close indeed to the exact wave-lengths of the red hydrogen ($\frac{1}{38710}$ inch) or the red cadmium ($\frac{1}{39659}$ inch) line. Thus, the space between any two successive lines of the 40,000 to the inch rulings corresponds practically exactly to the passage of two interference bands (two complete interference-band spacings) in red hydrogen or cadmium light. That this is true of the late Prof. Grayson's rulings labelled by him as 40,000 to the inch, has been proved by the writer by direct measurement against the interference bands, on the Comparator at the Standards Department. These more moderately finely spaced rulings are admirably resolved by the 1/15th inch dry objective supplied for the purpose by Mr. Conrad Beck. The lines, indeed, as seen through the fine-movement micro-

* Phil. Trans., A., 1910, *210*, 30.

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scope, are as clear as the interference bands in the interferometer of the Comparator, and the writer expressed hopes in his memoir to be able to carry out with their aid the determination, by this original method, of the exact number of red cadmium wave-lengths in the British Yard. Such a determination would, indeed, be quite simple and straightforward, with the proviso that an adequate supply of the rulings required for the stepping off process could be obtained.

The writer also hopes to use them as fiducial marks in connection with interferometric fine-measurement in general, and a General Interferometer, involving the same type of travelling fine-movement microscope as those (the pair) on the Comparator, is being constructed for him for the purpose at this moment.

The breaking out of the great war, and now the unhappy death of Prof. Grayson, have delayed the possibility of further work on the subject, and as doubtless other workers in high power microscopy are also at present unable to carry out their own particular researches for which the higher rulings are essential, the writer considers it desirable that the position shall be discussed at this Symposium of Microscopists.

The writer's suggestion is that the Symposium should address to the Governing Body or Council of the University of Melbourne a letter of condolence, expressing firstly the unanimous opinion of the great body of Microscopists and Scientific workers here assembled of the very great loss which the University has suffered by the demise of Prof. Grayson; and, secondly, the hope that the University will do all that is possible to ensure that Prof. Grayson's ruling machine shall still be available for the production of the " Grayson Rulings." It may be that Prof. Grayson had trained one or more members of his staff in his method, and if so it should not be difficult to arrange for the most highly desirable continued production of the rulings.

The writer took the opportunity of mentioning the matter to General Sir John Monash, the gallant Commander of the Australian Forces, and a member of the Governing Body and Council of Melbourne University, on his recent visits to London and Oxford on the conclusion of the War, and he kindly undertook to go into the question on his return to Melbourne. Possibly General Monash's relative, Dr. Rosenhain, whom we know to be interested so keenly in the subject from the microscopical point of view, and who has intimate connections with Melbourne and its University, will also be inclined to assist in carrying the subject further.

The continued production of the Grayson Rulings, especially those of the 40,000 to the inch spacing, is so important a matter that the writer has felt sure that the Symposium would wish him to bring it forward.

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THE TESTING OF MICROSCOPE OBJECTIVES AND MICROSCOPES BY INTERFEROMETRY.

By F. Twyman.

My firm has no commercial interest in microscopes, and so far I have not succeeded in interesting any microscope makers in the methods of test I shall describe. We have, therefore, not done much more on the subject than to test a few microscope objectives, and these, although by makers of repute, not of high power. They show aberrations of wave surface not exceeding about $\frac{3}{4}$ wave-length for monochromatic light (wave-length 5461). It will be remembered that if aberrations do not exceed $\frac{1}{4}$ wave-length, the resolving power of an optical system is practically perfect. This was found by Rayleigh to be the case in certain cases calculated by him, and general experience shows it to be a sound rule.

The interferometer used for microscope lenses was a side issue in the development of other forms.*

An image of a monochromatic light source is thrown on a diaphragm which has a small hole. The light passes to a half-silvered mirror (Figure 1). A portion of the light is reflected from there to a concave mirror so situated that the diaphragm is approximately at its centre. From the concave mirror the rays are reflected, and a portion of the light passes through the half-silvered mirror, and is focussed on the eye of the observer. The light which, on meeting the half-silvered mirror passes through it, proceeds through a compensating plate as in the Michelson Interferometer; then through the objective under test. The rays pass on through the image, and are reflected back on their own path from a concave mirror. Eventually the two beams of light combine at the surface of the half-silvered mirror, and pass on together to the eye. In these circumstances interference effects are observed which appear to the observer as if located on the back lens of the objective under test, and which represent a contour map to a scale of half wave-lengths of the aberrations of wave surface produced by the objective under test.

If desired, an entire optical instrument, such as a microscope, can be tested, in which case the arrangement is as shown in Figure 2.

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* Described by the present writer in the *Phil. Mag.*, Vol. XXXV., January, 1918, "Interferometers for the experimental study of optical systems from the point of view of the wave theory."

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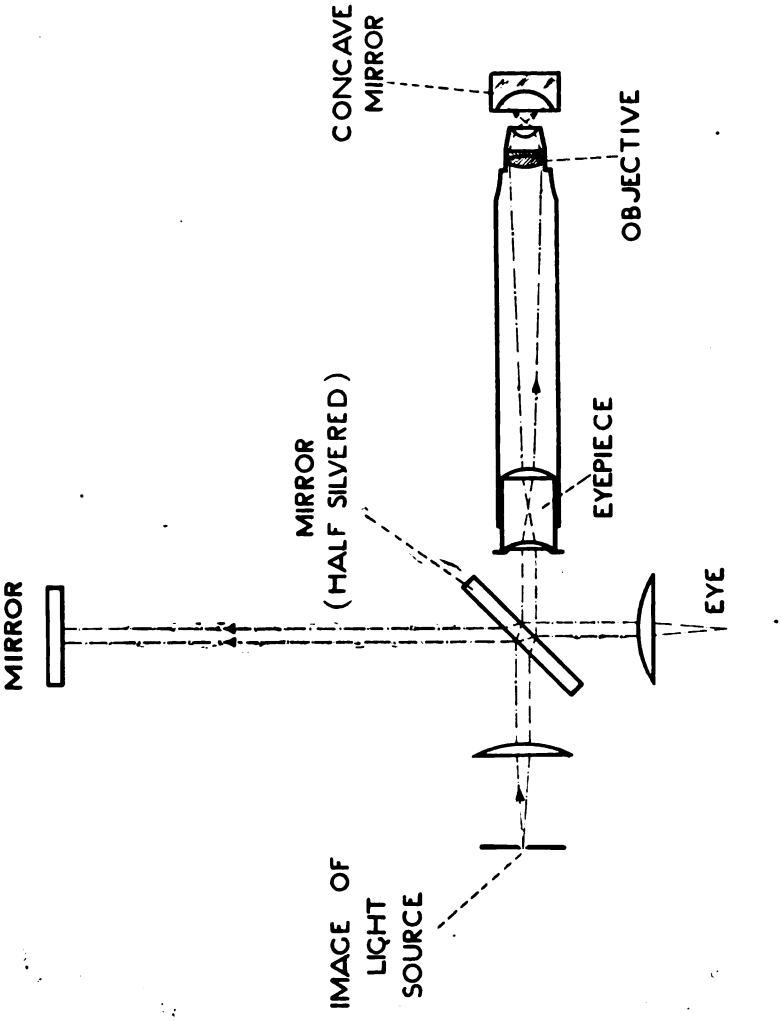

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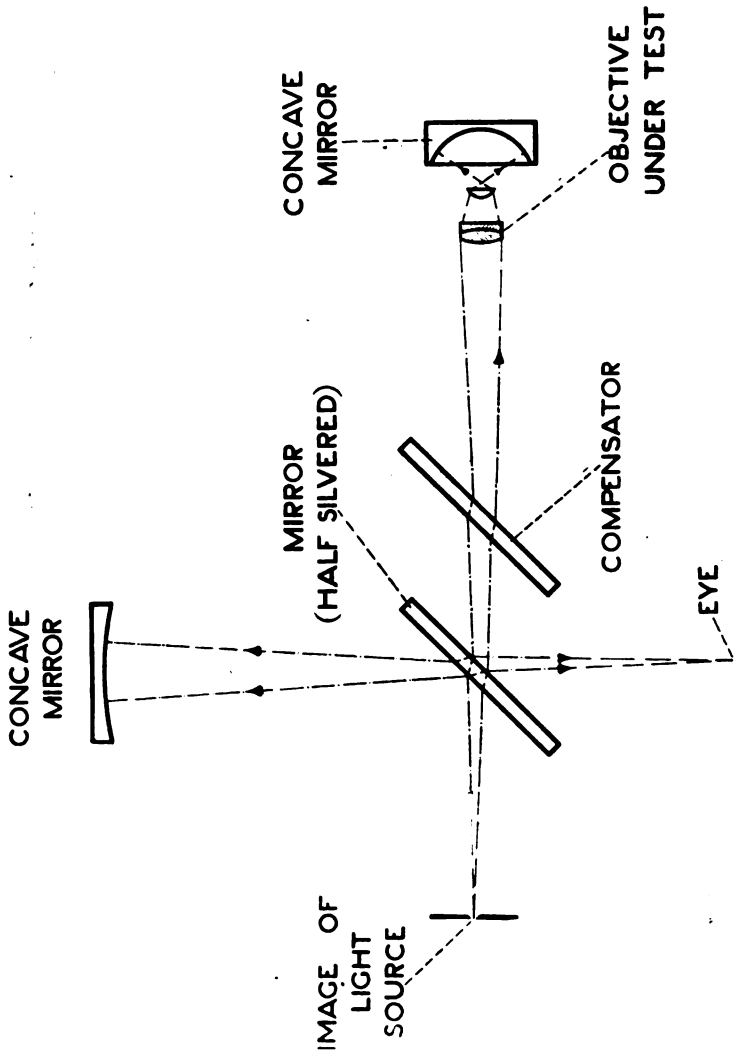

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AN ACCURATE METHOD OF OBJECTIVE AND SUBSTAGE CONDENSER TESTING.

By H. Hartridge, M.A., M.D.,
Fellow of King's College, Cambridge.

Preliminary Communication.

The methods of objective testing at present in use do not give quantitative data, and depend to a great degree on the keenness of vision, skill and memory of the observer.

A method which does not suffer from these defects consists in measuring with a suitable micrometer the position the image pattern when different parts of the objective aperture are used. If the lens is perfect and in correct focus no movement of the image pattern occurs. If there is movement, however, and if the micrometer reading be plotted against the N.A. of the part of the objective aperture in use, then the graph thus obtained shows the aberrations that are present and their amount.

A suitable method of isolating objective apertures of given N.A. was obtained by moving by means of a graduated micrometer screw a slit-shaped aperture placed below an oil immersion condenser. The method of calibrating the micrometer in terms of N.A. has been previously described.(1)

The best eye-piece magnification was found to be about 100 diameters; this was obtained by a 2-3 in. objective and a ×10 eye-piece.

The glass plate micrometer proved most suitable for measuring the displacements of the image patterns.

The method of illumination has already been described.(2)

The typical graphs obtained for certain aberrations may now be briefly described.

Centre of Field.

Perfect lens (a) correct focus:—a straight vertical line; (b) incorrect focus:—a straight inclined line; (c) incorrect tube-length:—S-shaped line.

Imperfect lens (a) spherical aberration:—a sinuous line (not of regular S-shape), and never a straight line; (b) central astigmatism:—a different curve in one azimuth to that given by another.

(1) Hartridge, Journ. Roy. Micro. Soc., 1918, p. 337.
(2) Hartridge, Journ. Quekett Micro. Soc., Nov. 1919.

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Periphery of Field.

A straight vertical line indicates perfect lens in correct focus.

(b) An inclined straight line shows perfect lens in incorrect focus. If the inclination is different to that found at the centre, the difference shows the degree of curvature of field.

(c) A bent line denotes presence of aberrations:—disobedience of sine conditions, etc.

Experience shows that " performance curves " for the centre of the field show almost at a glance the aberrations present, and their degree. Interpretation of curves for the periphery of the field is more difficult.

Colour filters only have so far been used for obtaining approximately monochromatic light, a prismatic spectral illuminator would be a valuable addition.

It will be observed that this method of objective testing has been developed from the method of adjusting tube length described in a previous paper.(3)

(3) Hartridge, Journ. Roy. Micro. Soc., 1919, p. 119.

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REMARKS BY SIR HERBERT JACKSON, K.B.E., F.R.S.*

By the courtesy of the Chairman I was able to see in advance a great number of the interesting papers which have been prepared for this meeting to-day, and when I looked at them I discovered that practically everything that I intended to say was included in those papers. I have decided, therefore, that it would be better for me to be brief, and deal very generally with perhaps only two or three points.

I take it that one of the chief reasons for this Symposium is to consider methods for promoting the study of the microscope and methods for extending its use in science, in industries, and in education. I should like to mention first the position which we are in at the present day with regard to one of the most vital parts of the microscope, namely, the optical glass. I should like this meeting to know that through the enterprise of British manufacturers we have produced and we can produce optical glass in this country of a quality equal at least to the very best that was ever obtained from abroad. I should like also to say that I have had it from the manufacturers themselves that they are perfectly prepared to do their very best—and they have already shown that they can do it—to produce any glass which may be called for. There is a great deal yet to be done, not on their part so much, perhaps, as on the part of those whose duty it is to make investigations with the object of obtaining new glasses with optical constants differing from those which have been made hitherto, so that combinations can be made of even higher quality than those which we are familiar with in the best lenses that exist. I think also that it should be well known that, through the efforts of the Department of Scientific and Industrial Research and in other ways, mathematical investigation on methods of designing lenses are in progress, and I think we may look definitely from these investigations for results which will make a heavy demand again upon the skill and the enterprise of the manufacturers of optical instruments.

I will not speak, as I had intended to do, on some comparisons between the results of the work of British and foreign manufacturers, except to say that it is certainly true that we have produced optical trains in this country comparing favourably with any produced anywhere else, but we do not always produce them with that constant accuracy. I think it is fair to say that while, in the early history of the microscope we took the initiative, in later years there has been a tendency to follow rather than lead. At least, that is true of some of the chief developments of the instrumental part of the microscope. Now, what we have to do is no longer to copy, but to aim at improvements by independent research and invention. There exists at the present time, fostered by the Department which I have just mentioned, an all-round spirit of research and enterprise. Without elaborating the point, one can now express the hope that a bright promise of future development will not fail of fulfilment through lack of means on the one hand to attract the brains and skill which are abundant in this country, and on the other hand to

* *See above, p. 43.*

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make possible the large amount of experimental work which is needed and which of necessity cannot be made to pay except indirectly, and in the course of time. Unless we can get experiments of that kind made by the people in the factories, the hoped-for advances from the instrumental side will not be fulfilled, at least to the extent which some of us think and believe to be possible.

I turn for the moment to the point of view of education. The growing use of scientific instruments in industry definitely calls for some systematic education in the theory of them and in their practice. There has recently been created a School of Technical Optics under the Directorship of my friend Professor Cheshire. We may therefore look confidently to having opportunities afforded for a thorough and systematic education, now so much needed, in the subject of the microscope and its use. That need existed over 25 years ago, but I do not know that any marked efforts have been made to give the systematic education required. Take the difference between the subject of spectroscopy and microscopy. In spectroscopy the work of educating the student is carried out in a systematic way. There is lecture work and laboratory work, and I think the student of spectroscopy knows his instrument and his subject as well as it is possible to do in the time he is required to spend on it. It is difficult to believe that the student of microscopy ever had a chance of knowing his subject so systematically and thoroughly. Therefore I plead very strongly for the greatest possible support for Professor Cheshire, so that he may bring this question of education in the microscope to a really practical and successful issue. Of the many possible forms of propaganda, none is likely to have a better or more lasting influence in the direction of arousing interest in the subject and extending the use of the instrument. How many of us have seen people who begin with the microscope and abandon it very soon after taking to it, and in nearly all cases it has been due to this, that they have had nobody to show them how to use the instrument or to make them understand what the microscope is, what it is in theory and in practice, and they have often not been able to interpret what they see.

We have listened to an Address by Mr. Barnard which is very interesting to me, because I have had the opportunity of seeing his work, and I think he is to be congratulated on the scientific work he has done in extending the use of the microscope. But it is more than that. Mr. Barnard has that spirit of research and that spirit also of realising that there is to be interpreted in the microscope a great deal that has escaped observation, although it may have been seen dozens and even thousands of times. What I want to see is, in addition to the necessary lectures on the theory, the formation of classes in the use of the microscope where objects are studied at low powers and low numerical apertures, and at high powers and high numerical apertures, by transmitted light, on a black ground, and by opaque illumination; and each appearance critically examined and described.

There is a definite lesson as to how each type of image is to be interpreted. May I take one or two instances. If a well-known diatom, *pleurosigma angulatum*, is examined with an illuminating cone of not more than .3 to .4 N A , and with a lens like a 1 inch,

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by ordinary transmitted light, what is seen is a brown or yellow-brown object. I am not going into the theory or the details, because it would take too long, and I am speaking to experts who, I am quite certain, know perhaps better than I, what is the explanation of the brown colour. But how many people who have looked at it simply as an object have asked "Why is it brown?" If you take that same object with a black ground illumination and a low angle objective, using an illuminating cone of .4 numerical aperture, all you see is the outline of the specimen. Yet what a wealth of information is to be gained from an investigation of the inside of that outline; Mr. Barnard has well indicated that when he was speaking of work in connection with the yeast cells. If you raise that cone to .65 with a black ground illumination, with the same objective, the object then is a beautiful blue or violet colour. Raise it still higher and it gets nearer to a greenish colour, and if you put on a little higher angle lens with an immersion condenser, the object looks very nearly white; raise the angle still a little higher and the image is white. That is an illustration of why every change should be explained and interpreted. Take another illustration: *tous-les-mois* starch grains mounted in water. With a black ground and an objective of a numerical aperture of .26, it is really a pretty object. The grains are nearly all pearly white, and the concentric rings can be seen quite well. If you keep the same objective, but raise the numerical aperture of the condenser, all the beautiful light goes, and nothing more than a mere outline can be seen; it looks like a little ring of light with nothing inside. Raise the aperture of the objective and use an immersion condenser, and you begin to see a little more showing up inside, and that is the first indication of the existence of a structure there. I should like the same thing to be taken with an opaque illuminator and examined. Opaque illumination, except in the examination of metals, has not had the attention paid to it that it should have because we have not laid sufficient stress on the necessity of looking at the object from all points of view, so as to decide by a careful comparison of the appearances in every possible form of illumination, the correct and proper interpretation. The student might be encouraged to go through a systematic course of theoretical and practical microscopy, applying what he learns in lectures to the study of objects of comparatively well-known structure by their examination with optical systems of increasing power and with various forms of illumination until he has gained a real knowledge of what can be revealed by the microscope and of what are its limitations. With this experience he would be in a position to proceed to research work equipped with sound theory and the fundamental practical knowledge necessary for the interpretation of what he sees and the avoidance of hasty judgment through incomplete observations.

If we could look forward to educational work somewhat on these lines in the future, people who wanted to study microscopy would find there was a great deal of valuable work to be done in extending the use of the instrument. The brilliant work which Mr. Barnard is doing in connection with ultra-violet light and increased resolving power cannot but help us very much in interpreting many things which we have seen but have not understood.

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The following papers are extended descriptions of exhibits shown before the meeting.

NOTE ON LIGHT FILTERS FOR THE MICROSCOPE AND PHOTOMICROGRAPHY.

By Lt.-Col. Gifford.

As far back as 1894 it was found that a solution of malachite green in glycerine absorbed all the visual spectrum except a broad band in the region of the F line of the solar spectrum, and a narrow red band near B (J.R.M.S., 1894, pp. 164-7), and that such a solution placed in a glass trough was eminently effectual as a light filter for microscopic use, especially when the red band was removed by inserting a piece of signal green glass into the fluid.

The year following, a screen similarly constructed, but with a solution of methyl violet for use in photomicrography, was described (J.R.M.S., 1895, pp. 145-7). In recent years it has been found that peacock-green glass possessed the same properties as signal green to a greater extent, and the use of the latter has therefore been dropped.

Instead of the glass trough with the signal green placed in it, the form these light filters have recently taken is as follows:—Discs of peacock-green glass about 0.06 in. thick and of diameter to fit into the substage condenser are cut out. On these discs are built up cells, using gold size and soft metal rings, or the former alone, just like those made for mounting microscopic objects in fluids. If a metal ring is used, then a coat of size must be given to the top of it and be allowed to dry. Then a final coat must be placed on that and allowed to get tacky. Then place rather more than sufficient dye solution in the cell near the edge. The glycerine will cause it to stand up beyond the top of the cell. Take a clean glass cover, make contact with the tacky gold size at a point nearest the drop of dye. The point of contact will act as a hinge. Now allow and assist the cover to fall until in contact with the gold size all round the ring. While the cover is falling and this contact is extending, the dye solution will flow forward and out in a wave. When contact is made with the top of the cell all round, take any blunt instrument and press the cover down in the middle until still more dye flows out. While this is being done adjust the cover on the ring if necessary, by the direction of the pressure. Quite a considerable pressure may be used, cover glasses are very flexible. When enough dye has passed out to leave the cover slightly concave, and you are assured that the adjustment is correct, suddenly remove the pressure. Pneumatic action will at once take place, owing to the resilience of the indented cover, and the edge of the latter will adhere so tightly to the gold-sized ring that it is possible to wash under the tap with a full stream of water at once. If made as described, the cell will not give out. Light filters made in this way are shown; one of them has been made and used for more than 20 years.

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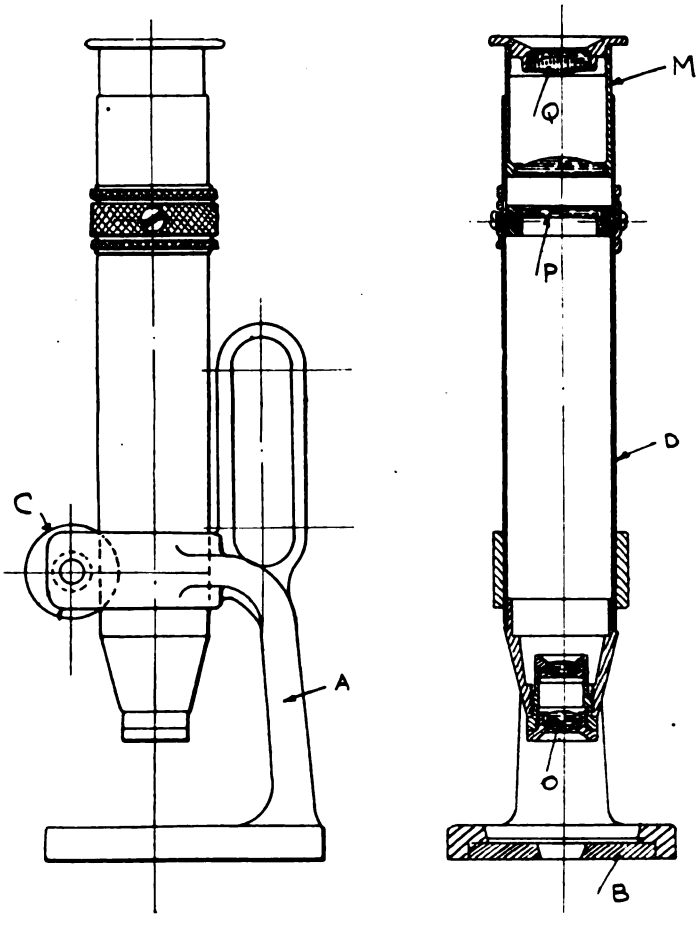
MICROSCOPE FOR MEASURING BRINELL IMPRESSIONS.

(Constructed by the Société d'Optique et de Mécanique de Haute Précision, Paris.)

The apparatus consists of two principal parts: the microscope properly speaking, and the limb or support.

The microscope itself comprises a mount D, carrying below an objective O, and above a micrometer P and an eye-piece Q. The objective is aplanatic and achromatic, and yields a linear magnification of 2.5. The micrometer has a length of 20 mm., which is divided



into 160 equal parts; numbers from 0 to 8 are marked every 20th division, so that a diameter of 8 mm. maximum can be measured within 1/20 mm. The positive eye-piece imparts to the whole system a total magnification of 21. The eye-piece rests in a small mounting M, which can glide in the tube D for adjusting the eye-piece with respect to the micrometer.

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The support A consists of the foot, a mount, a split collar provided with a clamping screw and a handle. The microscope fits with gentle friction into the collar, so as to be definitely adjustable with respect to the impression to be measured; it is then fixed in that position by means of a screw C. In the base of the support is encased a disc of fibre B, which is provided with a central aperture through which the impression to be measured can be examined. This fibre washer, as shown in the annexed diagram and in the model, may be replaced by a washer of suitable shape, so as to be adaptable to the piece to be examined by the microscope. The microscope weighs 0.390 kg.; the mahogany case weighs 0.650 kg.

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THE DAVON PATENT MICRO-TELESCOPE AND SUPER MICROSCOPE.

Exhibited by F. DAVIDSON.

This apparatus combines in standardised and instantly interchangeable form the functions of the microscope, telescope, camera and projecting lantern for laboratory, educational and industrial purposes.

The principle employed is the utilisation of an " air " image of a more or less distant object projected to the plane of the microscope stage by means of lens attachments which are inserted into the " Abbe " rim of the microscope stand, and then using the microscope itself as an eye-piece.

Three different attachments are brought into requisition, viz. the long focus attachment, the short focus ditto, and a micro object glass forms the third. The first transforms the microscope into a telescope with a range of vision of from six feet to infinity, and magnifications of 20 to 50 diameters. The second is used for objects which, by reason of their size or shape, cannot be examined on the stage of the microscope, such as minerals, metal fractures, etc., the visual range being from three feet to one foot from the stage of the microscope and magnification from 30 to 90 diameters. The third in combination with the microscope itself forms the super microscope. Magnifications of from 75 to 150 diameters with working distances of from four to two inches or of 1,500 diameters with working distance of $\frac{1}{4}$ in. are characteristic features.

Either attachment may be used for photography. With the first, photographs have been taken at distances of 6 feet and 70 miles, with the same combination; with the second, insects at from 18 ins. to 24 ins.; and with the third attachment, photomicrography of a wide variety of subjects at various magnifications from 1 to 3,000 diameters with excellent results.

The outstanding feature of all views and all photographs is the very great " depth of focus." This is so good that everything is shown in apparent stereoscopic relief.

The principle of photography with either attachment is the same, and consists of substituting a camera for the body tube of the microscope and virtually using a microscope objective as the eye-piece. No long extension camera is therefore necessary, exposures are shortened and vibration minimised in high power photomicrography. Photographs of Himalayan Peaks 60 miles away, and blood corpuscles at a magnification of 3,250 diameters have been taken in a $\frac{1}{4}$ plate without more than the ordinary extension.

The illuminant is arranged in an optical lantern with a 4 in. condenser and a supplemental condenser in a mount which fits the " Abbe " rim of the microscope. For projecting light on to a more or less distant object the 4 in. condenser is used alone. For photomicrography the supplemental condenser only is used, while with the two in combination effective micro-projection may be done without any accessories.

It is impossible in a briefly outlined description of the apparatus to indicate the wide variety of uses to which the apparatus lends itself, and it is no exaggeration to say that a new and wider field of observation and utility is opened up in many directions.

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DISCUSSION AT SHEFFIELD.

Tuesday, February 24th, 1920.

At a meeting of the Sheffield Association of Metallurgists and Metallurgical Chemists held at the Royal Victoria Hotel, Sheffield, on Tuesday, February 24th, 1920, further discussion took place on those papers presented at the Symposium at London, on January 14th, which dealt with the use of the microscope in Metallurgy and Metallography.

The meeting was held in co-operation with the Faraday Society and it was attended by members of other local bodies and by the members of the local sections of the Institute of Metals and the Society of Chemical Industry.

Mr. J. H. S. Dickenson, President of the Sheffield Association of Metallurgists and Metallurgical Chemists, was in the chair and he presided over a large audience.

The CHAIRMAN, having explained the objects of the meeting, called upon **Dr. F. C. Thompson, Mr. T. G. Elliot, Mr. J. H. G. Monypenny** and **Mr. F. Atkinson** to introduce briefly the papers they had contributed to the Symposium in London. Other papers were distributed in proof form.

DR. THOMPSON'S paper was entitled "The High Power Photomicrography of Metals."

SIR ROBERT HADFIELD and MR. T. G. ELLIOT'S paper was on "Photomicrographs of Steel and Iron Sections at High Magnification."

MR. J. H. G. MONYPENNY'S paper was entitled "Some Notes on the Metallurgical Photomicroscope."

The paper by MR. LESLIE AITCHISON and MR. F. ATKINSON was entitled "Metallurgical Microscopes and their Development."

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Discussion.

Dr. W. H. Hatfield did not think that there was any point on which he joined serious issue with the authors of the papers read that evening. Mr. Monypenny said that many people used the microscope and did not properly understand it. That was so. But looking at it from another point of view, there were people who regarded the microscope as a tool and looked to the manufacturers and the optician to further extend its usefulness. That was his position, and, generally speaking, the position most metallurgical investigators would take up. From that point of view one could tell the people who were making a speciality of the microscope what the metallurgist wanted. We might first of all tell them what we could do. From his own metallurgical experience he could obtain delightful microphotographs under ordinary conditions, and with ten magnifications get excellent empirical microphotographs. This was also the case with 50, 100, and up to 1,000 magnifications—excellent, almost perfect definition could be obtained. Beyond 1,000 diameters, however, we could not do so, and that was an essential thing to put before the people who were out to assist us in the use of the microscope.

There were a whole series of problems awaiting adequate solution, including the recrystallisation of cold-worked material, and solutions could only come when we have better facilities for definite and accurate information as to the internal architecture of the material at magnifications well above a thousand. We had produced very pretty photomicrographs up to three thousand diameters—Sir Robert Hadfield has produced excellent ones up to eight thousand—but these magnifications did not give us much more information than we could obtain by a clear definite picture at a thousand. If the Symposium had brought those facts before the notice of manufacturers of the microscope, it would have served a great purpose to metallurgists.

Dr. F. Rogers thought that the theory of lens design had been evolved much further than the theoretical side of metallurgy itself, heretical as that might seem. In reference to the high magnification work done by Sir Robert Hadfield and Mr. Elliot, he emphasised that whilst magnifications of 8 to 10 thousand were interesting as pictures, they did not contain any more detail; they were, in fact, of no greater value than enlargements. Nevertheless, he welcomed this high magnification as a progressive step, even though the result as regards detail was a negative one.

He put in a plea to metallurgists that they should make their photomicrographs bigger; if they were, an advantage would be gained. Such enlargements were better understood by the non-expert, even if perhaps as a record they were not so good. In regard to fine structures in the alloy steels—especially, for instance, in the study of temper brittleness—he would welcome anything which would give further resolution of detail. This information, he felt, was hidden away from them just at the limit of what the microscope could do. He thought the microscope would ultimately contribute to the solution of that problem.

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Mr. J. N. Greenwood referred to the difficulty of discussing the many points at issue. First of all there was the perfecting of the design of the optical system of the microscope itself. That was definitely a question to be tackled by the opticians. On the other hand there was the question of the use of the microscope, and in that connection there were very great improvements necessary in a good many cases. As regards the question of vibration, one speaker suggested that the people who supply the microscopes should supply some means of getting over this trouble. But the trouble could only be rectified by each user of the microscope himself, because at the various laboratories where the microscope was found the component vibrations were different. Sometimes it was the vertical which preponderated and sometimes the horizontal, and the question of the situation and the type of machinery close by had to be gone into before the vibration should be overcome.

As regards magnification, a good many metallurgists were expecting more from the microscope than was likely to be forthcoming in the near future. As far as he could see, unless there were some absolutely new development in the way of objectives we were not likely to get anything approaching the increase of magnification and resolving power which some metallurgists desired. Magnifications of 1,500 were now quite possible, and every one obtained them more or less easily. But to get at the bottom of such problems as brittleness and cold working we should have to get far beyond what we had been doing and approach molecular dimensions; even at ten thousand we were still a very long way from seeing molecules. It seemed to him that something like 100,000 would be nearer the mark, and he could not see how from the present system and using reflected light that we were likely to get anything of that order. If the opticians gave us 10,000, then they would have reached their limits with the present methods. He thought there was more prospect of getting information by examining other physical properties apart from or in conjunction with the microscope. He concluded by saying that during the past five weeks he had given more time and study to the microscope than he had during the last five years, so that in fixing attention on points like this, such discussions are invaluable, because few people had time to gather information of this kind.

Note added March 6th.—It has been suggested that I am pessimistic with regard to possibilities of higher magnification. I do not wish to convey the idea that I do not look for any improvement in magnification, but rather than in the two problems mentioned the probable improvements in the microscope will scarcely go far enough. On the other hand, there is an enormous field of utility for magnifications (with correspondingly high resolving power) of the order of 5,000, in defining the structures of special steels.

Mr. G. R. Bolsover said the papers resolved themselves into three types. A certain section dealt with the historical side, another with the utility of the microscope, and the third with the microscope as an instrument. The historical side was dealt with mainly by Sir Robert Hadfield in two papers. He suggested that in

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dealing with the work of Sorby that account could with advantage be extended to include not only the work of Sorby, but his life as well. In the case of a man who had done so much for science and incidentally for civilisation as a whole, we should have a permanent record of this man's birth, training, and career in detail up to his death, apart from the question of his work.

As regards the microscope as an instrument, he agreed that it was the optician's affair. There were many comments in the papers on the different forms of microscopes. His experience had been that there were many microscopes on the market capable of giving excellent results when properly used, but they were not made to meet the particular fads of individual workers. Results were dependent more on the individual than upon the particular type used. There was in use in his laboratory four different microscopes—one Austrian, one French, one modern, and one ancient British. It was possible to get good results from all of these. The two oldest were the Austrian and the old British. The latter was perfect in almost every respect, whilst the stage of the Austrian could be moved through quite a considerable angle in the direction in which it should be perfectly rigid. He did not think they need fear much from the superiority of the Austrian make of microscope.

With regard to stages, he uttered a word of warning—do not get a levelling stage. It was a distinct advantage to have an up-and-down movement of the stage in order to avoid altering the light sources for sections of varying thickness. On the question of light there were a number of elaborate schemes for lighting for visual work, but they got excellent results with the ordinary electric bulb with the interposition of a ground glass screen. One could get a light sufficient to show all detail, and it did not tire one's eyes. As to the source of light for photographic work, he was rather interested in some of the papers in which it was suggested that the arc was too uncertain a source and suffered from flickering. They had tried both the arc and the "Pointolite," but preferred the arc, and got excellent results from it.

Mr. Atkinson pointed out that the focussing arrangement for long distance work was one that required a great deal of attention. At times a considerable extension of bellows is required to take a photograph, and unless a really good apparatus for focussing was available, it was very difficult to get a fine adjustment.

With regard to higher magnification, one direction in which he anticipated this would be an advantage was in the disproving of certain theories at present in vogue with regard to crystallisation, but there was still a tremendous field to be explored with the facilities which were now available. Another difficulty with regard to higher magnifications was the question of polishing and etching. With the present method of polishing it was practically impossible to get a plain surface to examine, and when one came to etch the difficulties were increased. The difficulties were really enormous, and until they were removed there would be great difficulty in examining steels, let alone photographing them at high magnification.

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The Chairman: Dr. Thompson refers to the Reichert microscope, and says very good results can be obtained when the disc illuminator is used instead of the pair of prisms ordinarily fitted. Does he know whether such a microscope has been made by Reichert?

Dr. F. C. Thompson: Benedicks has adapted one himself for that purpose.

The Chairman: Another point is with regard to vibration, and regarding this I would point out that Dr. Rogers would not use a four-metres extension if his apparatus was established near a steam hammer. Usually in a works it is necessary to use a short extension for this reason.

Dr. F. Rogers: There is a good deal in that. I am glad that the discussion is touching on the question of vibration. It has been suggested to me that the whole apparatus should be afloat on water or oil. It seems to me a rather good idea, but I don't suggest that you should have to swim to it. I have not worked out the detail, but I think the problem will be ultimately solved in that way, perhaps combined with springs or india-rubber moorings.

Dr. W. H. Hatfield: Arising out of this discussion there is one thing I should like to say with regard to my experience. I have done a great deal of photomicrography, and for one period of something like six or seven years I used a Watson microscope. Now, that microscope cost about 50 to 55 guineas, whereas the Zeiss cost about 100 guineas. I produced well-nigh perfect pictures at 1,000 and slightly over. In fact, the work was equal to that given by the Zeiss, and I shall be glad to show anyone the slides. I mention this because so much has been said about the German manufactured article being better than the British, and I think it is only fair that we should put that on record.

Mr. L. Dufty drew attention to the different magnifications given in the various papers, and suggested that it would be a great improvement if standard magnifications were adopted. Another thing that should be stated in the papers was what objectives and eye-pieces were used. It would be a great advantage if these were given when stating the magnifications.

The Chairman: The matter of standard magnifications is mentioned in Sir Robert Hadfield's Introductory Address. The American Society for Testing Materials has issued a list of standard magnifications which, as far as my recollection goes, runs in fifties. It is open to every investigator to work to simple, round figure, magnifications.

Mr. L. Dufty: Yes, but you will see investigators often work in anything except round figures.

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The Chairman: I am sometimes ashamed of some which I see hanging in my laboratory which are marked " ×117.5," but these were taken 18 years ago, and we have now for many years worked to a few fixed round-figure magnifications.

Dr. T. Baker: Those of us who have had the opportunity of examining the work of old masters in the art of photomicrography I think will agree that they, with imperfect apparatus, turned out much more satisfactory work than many of us to-day do with a much more perfect equipment. A great deal depends on the operator, and a closer study of the construction of the microscope would assist him in avoiding the pitfalls into which a good many metallurgical microscopists are apt to fall. There is a great tendency to make the metallurgical microscope too complex; amongst the fittings to be avoided are levelling stages and centering nose-pieces; a centering stage is much better than the latter, since it can be much more substantially constructed.

As regards objectives, apochromats are without doubt a valuable asset to the skilled worker, but how many can distinguish between the image formed by a good achromatic and that given by an apochromatic objective, without the assistance of the inscription on the mount; then, again, by far the greater part of the work of a laboratory does not call for the use of apochromats.

As regards magnification, it is generally stated in the standard works on the subject that little if anything is gained by using magnifications greater than 1,000 times the numerical aperture of the objective, so that until the resolving powers of objectives are increased there seems to be little advantage in pushing magnifications much beyond 1,500 diameters.

As an illuminant the speaker prefers the direct current arc to the " Pointolite " lamp, in spite of the fact that the latter has several points in its favour, such as steadiness and constancy of brilliancy. The prism form of vertical illuminator appears to have fallen into bad repute; the speaker, however, prefers it to the cover-glass type, in spite of the fact that it reduces the numerical aperture of the object by one-half in one direction, a weakness which is not such a serious matter as many try to make out.

Mr. H. Wrighton said he had considerably reduced the flare in a 4 mm. .95 N.A. objective by blacking the inside of the mounts near the front of the objective, which were brightly polished. He produced further photographs of a very fine pearlitic structure, and said he considered that, taken at 8,000 magnifications, was better than the corresponding photograph of the same field at ×1,500, as the details of the structure could be more plainly seen. A Zeiss × 12 compensating eye-piece was used in obtaining the photographs at 8,000 magnifications. He submitted photographs of a long distance fine focussing adjustment he had fitted to his Zeiss-Martens horizontal microscope, and found to be quite satisfactory.

Mr. J. H. G. Monypenny, referring to the capabilities of different stands, said he had never met one to equal the large " Works " model made by Watson. He had used one of these stands fifteen years, and it was still in perfect condition. He had tried a number

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of other stands, including the Zeiss-Martens, but had not seen one to equal the Watson. Opinions differed as to the relative wearing qualities of British and German stands; there was no doubt, however, that the better quality British stands were good instruments, and would stand a great amount of use; at the same time they could be improved by using more suitable kinds of metal for the moving parts, such as pinions and racks.

With regard to objectives, the English achromatic lenses worked perfectly, providing they were used with yellow-green light, and with low and medium powers one could obtain results comparable with those given by Zeiss apochromats. For low power work they had the advantage of possessing a much flatter field than the apochromats, but they did not work well with blue-violet light. Some of the new apochromats made by Watson and Swift were, he believed, very good lenses, but he had not tried them. For the highest powers the apochromat was much superior to the achromat, though good results could be obtained with the latter.

Several remarks were made about fine focussing arrangements. Nearly all his work had been done with a vertical camera, and, being endowed with a rather long arm, he had not needed any extended arrangement for focussing. The arrangements he had seen have been rather a nuisance, and probably the worst was the one fitted to the Zeiss-Martens stand.

For very low power work he did not think any ordinary type of microscopic objective suitable if one required a large field. Some type similar to the Zeiss projection lens was much better; with such a lens one could easily obtain a field up to ⅝ in. diameter.

With regard to the use of prism or disc illuminators, in spite of what had been said, he believed the disc was very much better than the prism for high power work. Providing the structure was suitable and the detail in the section arranged in the right direction (that is, with respect to the prism), one could obtain very good photographs with the prism illuminator, but in most specimens, for example, of pearlite, the laminae were arranged at different angles in various part of the field, and it was impossible to arrange it so that each set of laminae was in the best position to be resolved. For low power work there was no doubt that the prism was superior to many individual discs on the market for the reasons given in his paper.

Reference was made in one of the papers to the impossibility of obtaining good contrast with medium power dry objectives, such as the 1/6th inch, owing to flare due to reflection of the incident light at the front surface of the objective. He had used a Zeiss 4 mm. apochromat for some years for metallurgical work, and found it quite easy to obtain sufficient contrast. It would be very inconvenient to have to use an immersion lens for such powers.

Several references had been made during the discussion to the various types of metallurgical stands. Many of the new fancy stands were no improvement on the old type, and very often they were much worse. In a metallurgical stand, the stage should have a coarse adjustment, but the fine adjustment should be on the tube. In any case, the milled head for the fine adjustment should not be fixed to a movable part of the stand (such as the stage), as, if so,

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the flexure due to the pressure of the hand might be sufficient to affect the focus of a high power objective. In this respect it might be mentioned that when using a 2 mm. immersion objective of N.A. 1.40 a movement of $\frac{1}{50,000}$ of an inch along the optical axis was sufficient to put the field out of focus.

With regard to Dr. Thompson's remarks on the halo produced round the fine detail in photographs at very high magnifications, while agreeing that such halos were produced, he thought their width was rather less than stated by Dr. Thompson.

Mr. Birch pointed out that by the use of different screens photographs were obtained which seemed to represent two totally different things. The whole process of photography should be understood besides the optical system.

Dr. W. H. Hatfield said that with regard to the standardisation of magnifications in his laboratory, they had found it helpful to standardise to 10, 50, 100, 500, and 1,000 diameters. It would be very helpful in studying the work of other people if the photographs were of the same magnifications.

Mr. J. N. Greenwood: The question of the size of reproduction also arises.

Dr. W. H. Hatfield: I suggest that the matter is worthy of consideration.

The Chairman: Such standards have been laid down in America.

Mr. T. G. Elliot: Sir Robert Hadfield has taken a great interest in the question of standard magnifications for photomicrographs, and he long ago decided to use standard magnifications in his own research laboratory. He took a practical interest in the work of the Committee of the "American Society for Testing Materials," which was responsible for drawing up the report on "Magnification Scales for Micrographs," which has already been mentioned this evening, and several of his suggestions were adopted and are included in the revised report, published in June, 1918. In that year, too, Sir Robert endeavoured to get the British Engineering Standards Committee to take up the subject in this country. After due consideration, however, they decided against it, because they felt it would be impossible, at that time, to standardise the lenses to be used in obtaining the magnifications, without which the standardisation of magnifications would be useless. It was also thought that this matter and the related one of the full-sized reproduction of photomicrographs might well be left to the Publications Committees of the various Societies interested.

The Chairman said that in his laboratory they had adopted 100, 250, and 750 as standard magnifications.

Dr. F. Rogers advocated the adoption of round-number standard magnifications for reproduction and report purposes.

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Dr. F. C. Thompson said it was at times very difficult to confine oneself to given magnifications. The Institute of Metals had brought out a list of magnifications seven or eight years ago, and authors of papers were requested to confine themselves to those standards, but no attempt appears to have been made by the Publication Committee to enforce these, and he did not think they were being observed now.

With regard to stands, in his experience the English stand was absolutely unsurpassed. They had some very old Beck stands at the University which had been subjected to extremely hard work, and even now those stands were in excellent condition. The same applied to geological and other stands by Watson's, which were being subjected to equally hard work. They appeared to be a distinct improvement on anything that foreign countries could supply.

With regard to objectives, the position was not quite the same. For lower power English objectives were most admirable, but he agreed with Mr. Monypenny that above one-sixth the Zeiss was much better. Dealing with illumination, the arc lamp, if it was working well, did quite admirably. Small arcs, however, were very unsatisfactory. If it were not for the increased amount of attention required, the ideal illuminant was the lime light. One got large area of illumination of high actinic value if one took the necessary trouble.

A Member remarked that if a standard for magnifications was fixed there should also be a standard of objectives for each magnification.

The Chairman: On this matter of standard magnification this Association might very well have the views of all our members using microscopes ascertained and a memorandum prepared.

Mr. F. S. Spiers said that an important factor in determining the size of reproductions was that of cost. Anyhow, that placed an added difficulty in the way of standardisation. With the permission of the meeting he would like to bring up the subject before the Council of the Faraday Society, and perhaps some steps might be taken in the direction of standardisation. There were one or two things mentioned in the discussion in London which he thought it of interest to bring forward, notably the suggestion to form a standing committee to undertake proper tests of objectives now being manufactured. It was hoped that would settle once and for all the question of the merit of British objectives.

The Chairman: It appears that members of our Association are not quite unanimous on certain points. In the first place, as regards the question of disc *versus* prism illumination. I may have been unfortunate in my experience of prisms, but I always find that I can get better photographs with even ordinary covered glasses than from any prism, and, judging not only by my own results, but by those of my friends, I must say the glass disc illuminator is much to be preferred to the prism. The other point on which there is a sharp difference of opinion is with regard to illuminants. I have

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found the " Pointolite " extremely useful and, if properly used, it gives excellent results. It gives a very steady and strong illumination, and may be used for everything except screen projection, when the greater power of the arc lamp is required.

I think rather too much has been said to-night with regard to photomicrography, and too little about the use of the microscope for purposes of examination and study, especially at high powers. Actual research work is not done by examining photomicrographs, but by prolonged visual inspection of structures under the microscope. It is rather the tendency nowadays to take a photograph and hardly look at the specimen at all; but, after all, photographs are only imperfect illustrations necessary for reports and publications.

As regards the present indifferent construction of microscopes, I consider that it is for the metallurgical engineer, who should know what he really requires, to design the mechanical details of his microscope, leaving the optician only to deal with the optical system. Further, with regard to existing microscopes, I quite agree that English microscopes have been very unfairly condemned in comparison with Continental instruments, although as regards objectives English makers do not seem to be able to keep up to the same standard of excellence as Continental makers, but they occasionally turn out lenses which are as good as can be obtained anywhere. Then, as regards enlarged photomicrographs, I must say that I fail to see any point in enormously high magnifications obtained by this means. Such photomicrographs at, say, 5,000 diameters magnification, give no information which cannot be obtained from a photomicrograph at 1,000 diameters.

Dr. F. Rogers: As an enlarged photograph it is of some use.

The Chairman: Yes, as a picture for hanging on a wall. You can, of course, go up to enormous enlargements by the use of a lantern, but this only assists by permitting more people to see the photograph at one time.

Mr. T. G. Elliot: A photograph taken at 5,000 magnifications has this advantage over an enlargement, that before taking the photograph, you select your field at this magnification, and, as we say on page 5 of our paper, " we consider this an important point." We quite agree with Mr. Dickenson and other speakers who have criticised the use of very high magnifications, that nothing new has been learnt from them; although we submit that inasmuch as they do enable one to see the details of the structure easier, they have this important advantage over photographs taken at lower magnification. It was partly because Sir Robert Hadfield believed that we had got as far as was practicable with the apparatus available, that he suggested a Symposium on the Microscope, in the hope that it would focus attention on this point and lead to increased effort to obtain apparatus which would open up new fields of investigation.

Dr. F. C. Thompson, replying to the discussion, said that as the wave-length of light decreased the resolving power was increased. Up to the present ultra violet light had been unsatisfactory with metallurgical specimens, though there was no obvious reason why

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this should be so. With regard to Mr. Monypenny's criticism of the diameter of the halos, he had formed his conclusions on the ordinary laws of optics, and there was no very obvious reason for departing from it.

Mr. J. H. G. Monypenny said he was quite in accord with what had been said with regard to magnification, that the limit is reached at 1,500 diameters. The only advantage in photographing above 1,500 (apart from photographs for reproduction purposes—in which case enlargement is sometimes desirable), might be in the case of a man whose vision was not as good as it might be, or who did not wish to tire his eyes examining every detail.

The Chairman, in concluding the meeting, said: We are very glad to have had the opportunity of discussing in Sheffield the papers on microscopy which were recently read before the associated Societies in London, and I think I may say that this Association is grateful to Sir Robert Hadfield for making the suggestion that such a further discussion should take place. If, and when, the Faraday Society has another Symposium on some other subject, this Association will, I am sure, be pleased to arrange for another joint local meeting on the lines of that held to-night.

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ADJOURNED DISCUSSION IN LONDON.

April 21st, 1920.

The Royal Microscopical Society held a special meeting on April 21st, 1920, in the Rooms of the Society at 20, Hanover Square, London, W., in conjunction with the Optical Society and the Faraday Society, to discuss the papers presented to the Symposium which dealt with the "MECHANICAL DESIGN AND OPTICS OF THE MICROSCOPE."

Professor John Eyre, President of the Royal Microscopical Society, who was in the Chair during the first part of the proceedings, opened the Discussion with the following remarks :—

The object of our meeting this evening is not to initiate a fresh discussion on the microscope, but to continue the work which was commenced at the Symposium held in January last. The volume of communications which was simply poured upon the Symposium was so great that it was impossible to discuss more than a very few of them, and, indeed, many papers were only presented in abstract, but in order to correlate the views of all the workers in this branch of science, we are arranging a series of short meetings in which specially selected papers can be discussed, and the results of the discussion recorded for publication. During the course of the evening my two confreres, Sir Robert Hadfield, President of the Faraday Society, and Mr. R. S. Whipple, President of the Optical Society, will each take the Chair for a period, in order that the members of their Societies may feel that they are adequately represented.

The Chairman then called upon **Mr. J. E. Barnard** to give a GENERAL SURVEY of the subject (*see* page 37), after which abstracts of the following papers, read at the original meeting, were presented by their respective authors:

THE MECHANICAL DESIGN OF THE MICROSCOPE.

(*a*) *General.*

PROFESSOR F. J. CHESHIRE, C.B.E., "The Mechanical Design of Microscopes."

MR. CONRAD BECK, C.B.E., "The Standard Microscope."

MR. F. W. WATSON BAKER, "Progress in Microscopy from a Manufacturer's Point of View."

MR. POWELL SWIFT, "A New Research Microscope."

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(*b*) *Metallurgical.*

Dr. W. Rosenhain, F.R.S., "The Metallurgical Microscope."

Professor Cecil H. Desch, D.Sc., "The Construction and Design of Metallurgical Microscopes."

Mr. E. F. Law, "The Microscope in Metallurgical Research."

Mr. H. M. Sayers, "Illumination in Micro-metallography."

(*c*) *Petrological.*

Dr. J. W. Evans, F.R.S., "The Requirements of a Petrological Microscope."

Sir Robert Hadfield, F.R.S., in taking the Chair during the reading of the metallurgical papers, said:

I do not intend to take up much of your time, but should like to say in a few words how very gratified I feel to see this important gathering continuing the work we tried to do a couple of months ago. We then had something like 40 papers presented, and as, of course, it was quite impossible to do more than touch upon the fringe of the discussion of them, I may also add that out of that large gathering in the Rooms of the Royal Society we have had a continuation of the same work in the cities of Sheffield and Glasgow. That will show you that we did really stir up not only the metropolis, but also the north and the far north. As I am taking the Chair during the reading of the papers in the metallurgical section, I would like to say how very important we find the microscope as regards metallurgical operations and investigations. My friend Mr. Barnard has said that we do not think sufficiently of resolution and that we are rather too fond of magnification. I still have a little feeling for magnification, but cannot help thinking that we shall, aided by resolution—the double resolution of the microscope and our own resolution—find out improved methods of handling steel. That is a matter I am specially interested in. The more one studies the structure of iron and steel, the more fascinating it becomes. To use an illustration in which I have been concerned very much during the war, *i.e.*, the production of the large calibre armour piercing shell, we could not really have obtained a shell of the requisite quality without the use of the microscope. When one considers that the 18-inch gun carried a projectile with a muzzle energy of 150,000 foot-tons, one can imagine the tremendous stresses which occur when that shell is suddenly brought to rest by the armour attacked, and yet it must not break. Out of those war researches are proceeding further investigations which will apply that information to the arts of peace, and I do not think it will be found that we have wasted our time. We in England were not behind, but we wanted stimulating a little, and a great deal of investigation work was carried out during the war which would not have been done otherwise, because in times of peace the money could not be found.

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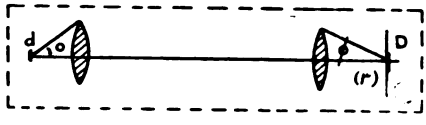
DISCUSSION.

Commander M. A. Ainslie, R.N.: With regard to design, the principle of the optical bench seems to me exactly the principle needed in order that you may build up in bits the apparatus you want for any particular research, so that everything may fall naturally into alignment. Each piece of apparatus should be on a separate saddle of its own. I would even have the eye-piece on a separate saddle, with a separate coarse adjustment of its own; this may sound revolutionary, but I believe it to be perfectly sound. Then, again, I think we ought to have a longer range to the draw-tube; as a rule, it is quite insufficient, especially when high power dry objectives are in use. An ordinary dry 3 mm. objective requires a change of about 20 mm. in the tube-length to compensate for a change of .01 mm. in the thickness of the cover glass; and although objectives of lower power are less sensitive, objectives of low power and large aperture are not very easy to obtain.

With regard to the size of illuminant required in photomicrography, whether of metals or of other objects, this is settled by a very simple relation. If d be the diameter of the light-source, and D that of the illuminated area on the object slide, and if θ be the



angle made with the axis of the extreme ray entering the optical system and ϕ that of the extreme ray falling on the object, the latter being supposed in a medium of refractive index μ, then we always have

$$d \sin \theta = \mu D \sin \phi,$$

which is, of course, merely the well-known "optical sine law"; it really amounts to saying that the product of the diameter of the light-source into the N.A. of the collecting lens is equal to the diameter of the circle of illumination on the object, multiplied by the N.A. of the condenser. You cannot get away from this relation; it settles once for all the diameter of the illuminated field, and it is true for any optical system whatever between the light-source and the condenser.

If you are going to use a metal filament lamp, you are confronted with one of two things; either you are going to project an image of the filament on your object, or else you are going to project this image into the plane of the objective aperture, filling it irregularly; a state of things which Professor Conrady long ago showed to be incorrect. The diameter of the filament is far too small, having regard to the relation I mentioned just now; and of course one does not want an image of the filament on the photograph.

With regard to the intensity of the arc, what decides the exposure is the intrinsic brilliancy and not the total power of the arc. As to the heating effect, I have used a 25 ampere arc within

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1¼ inch of one of the solid glass rods supplied by Messrs. Beck, for half an hour at a time, without the slightest damage to the glass, and I am inclined to think that this " bogey " of the danger to your collecting lens is somewhat over-rated.

Mr. C. Beck: Has Commander Ainslie tested the amount of light lost by absorption from glass to glass. Is it 75 per cent.?

Commander Ainslie: Yes, of course, a great deal of light is lost. It was a question of the capability of the glass to withstand heat. It is a question of the size of the illuminant. I have seen a piece of ground glass as the source of illumination instead of the crater of the arc itself.

Mr. Maurice Blood: You can use a large collecting lens.

Commander Ainslie: But you will not get more light, because it is the intrinsic brilliancy of the light that counts.

Dr. R. Clay: The feature that pleases me most in the microscopes that Mr. Beck has shown is the provision that he has made by which one can start with a simple form and gradually build it up. I have been advocating this for some time, and I am very glad to see it is accomplished here. That a student who has not too much money can commence with an inexpensive instrument and add to it as he goes along, and as he feels the necessity for and understands the use of improved apparatus, is a very great advantage.

I was very much interested in Commander Ainslie's formula connecting the area illuminated by a substage condenser and the aperture of the condenser. I think it is one of the most important things that has been brought forward during this Symposium, because there is quite a lot of nonsense talked about the illumination of microscope objects, and that formula puts the whole in a nutshell. I was also interested in the paper on the illumination of metallurgical specimens, as I think it is possible with a prism that I devised some time ago for another purpose to give the 50 per cent. illumination that has been asked for in that paper.

Mr. W. R. Traviss: I should like to mention that it is over 35 years ago since I introduced to Messrs. Swift and Son a microscope on the lines of the one that the last speaker has said he would like to see, viz., an instrument that could be commenced in a small way and gradually built up as time goes on.

The simplest form had a firm tripod, of which the toes of the legs were cork-filled to give firmness. The stage was a cut-open form recommended by the late Dr. Dallinger and Mr. E. M. Nelson. The coarse adjustment was made by the body sliding in a cloth lined fitting. The screwed holes for the attachment of the limb or arm to the stage were made a standard distance from the optical centre, so that a coarse adjustment with rack and pinion movement could be exchanged. The side edges of the stage were grooved for the vertical movement of a mechanical stage or roller sliding bar which

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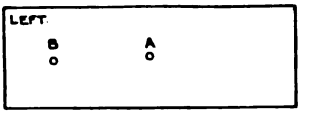
could be easily slipped on and off. The under-stage tube was fixed to a plate; this could be replaced by a centering motion, rack and pinion sub-stage. The sliding draw-tube could be replaced with a rack and pinion draw-tube divided into mm.

Another addition which is added to a small portable microscope, and would be useful to all plain stage microscopes, whoever the maker might be, is a very simple and efficient finder, and is standardised as follows:—

Each maker has a 3 × 1 in. piece of metal 1 mm. thick. At equal distances from the ends and sides is made a small hole (A) 1 mm. diameter, and another hole the same size, made exactly 1 in. distance from the centre hole and equal distance from the sides (B), thus:—



When an instrument is assembled and completed ready for sale the above plate is placed on the stage of the microscope resting against the sliding bar or mechanical stage, or a mechanical square; then with a 2/3rd or 1 in. objective the hole A. is brought into the centre of the field of the eye-piece; the metal 3 × 1 is held firmly by the stage springs or clips, and a small sharp drill is passed through the hole B and a few twists given, which will make a drill mark on the stage. This is then filled in with Plaster of Paris, thus giving a white dot over a black stage.

Now suppose we have a scattered slide, and some part (or parts) has some object of special interest which one wishes to find quickly at some future time—all that is needed when the object is squarely on the stage is to make an ink dot on the slide exactly over the white dot on the stage. Other dots can be made if needed, and marked A, B, C, etc. Then for the future all that is necessary is to place dot A, B, or C over the white dot on the stage, and the desired part is in the centre of the field of the eye-piece.

With regard to Dr. Evans's paper, he has specially mentioned crystals, but I do not think any instrument is so efficient for examining minute crystals as the one introduced by Mr. Allan B. Dick. In this instrument you can introduce a minute crystal on the cross wire, and it does not alter its position at all.

Dr. J. W. Evans: No one appreciates more than I do its valuable qualities, but it is impossible to apply the methods devised by Professor Beck for the study of interference figures to a microscope with rotating nicols, at any rate without very considerable modification, and in the second place the small upper Bertrand lens cannot compare in convenience and effectiveness for the examination of the interference figures of minute objects with a Beck lens placed above the eye-piece, in conjunction with a diaphragm placed in the focus of the latter.

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Col. J. Clibborn: We have heard to-night an immense amount of detailed information as to what is desirable, but nobody has suggested yet the means by which we may attain our object. I do not think there is any doubt that what is desirable is that we should, at all events, have one standard microscope which will fill the conditions that have been mentioned. We should at all events have one pattern—it is possible that we may require other patterns—but we at any rate require one pattern of standard microscope, because it is only possible to manufacture in very large quantities. These instruments cannot be manufactured cheaply, even in large numbers, unless you have suitable machines, and the question is how are we going to arrive at this condition of things. I do not think it can be done by separate manufacturers, because it is not possible that the patterns will all agree. The manufacturers might all join together and form a combination, and perhaps it might be done in that way, but I think the best way is what I suggested 12 months ago, namely, that a Committee should be appointed of the ablest men interested in the question, inside and outside the Society, to devote themselves to the design of the standard microscope. It should undergo as much criticism as can be brought to bear upon it, and then we should endeavour to get an instrument made and tested. If we do not, I am perfectly certain that the manufacture of the microscope will leave this country and go to the Continent.

Dr. J. R. Leeson: An important question is that of price. I have been trying for four years to fit up my little laboratory with microscopes, but I cannot get them; at least, if I can get them I cannot find the heart to pay for them. Scientists are not rich people, and if you are going to popularise the microscope, you must have an instrument that is within the reach of the ordinary individual. If you do not, then the trade will again leave this country.

Dr. R. Mullineux Walmsley: The last speaker and the last speaker but one have referred to matters with which I have been somewhat associated through the British Science Guild. A Committee has been proposed here to-night, but I would like to inform the proposer that the work he suggests has already been done. The British Science Guild first of all invited well-known users of microscopes to schedule their requirements. Having collected and collated these schedules, we asked the manufacturers to join the Committee and tell us whether it was possible from their point of view to produce microscopes which would fulfil their requirements. Eventually by the combination of the scientific men who were using the microscopes and of the manufacturers, we drew up and published specifications for three or four standard instruments for different purposes. We were in the middle of the Great War at the time, and the object was to see whether manufacturers would consider placing such instruments on the market, when peace came, with such added modifications as the progress of time might render desirable. The question of price was not overlooked, although I do not know that the prices we put down in 1917 can be held to at the present time.

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The evidence of the work is on record, both in the *Journal of the British Science Guild* and the Royal Microscopical Society, and I fancy that the manufacture of both instruments exhibited to-night were to some extent influenced by the specifications prepared by the Committee.

Mr. Conrad Beck said that the standard instrument made by his firm was made to the specification of the British Science Guild Committee, but the larger one, made by Messrs. Swift, was quite a different matter. The latter was more of a special research type. He certainly welcomed the suggestion that a small sum of money should be put up to assist in manufacturing microscopes. But what was meant by a small sum? In some instances upwards of £20,000 had been spent in tools and machinery; Messrs. Watson and his own firm had each expended an enormous amount of money on machinery and tools which it was hoped in course of time would be found advantageous to microscopical work, and if a small sum meant something of this nature it was an excellent proposition.

Mr. Watson Baker: The microscope which our firm has made according to the specification of the British Science Guild is not here to-night, but I am glad to take this opportunity of saying that we should welcome any members of the Royal Microscopical Society to our works to see exactly what is being done.

I believe that Col. Clibborn himself would be pleased to see that microscopes are being made by machinery in a manner not hitherto done in this country. It has taken us 12 months to put up a new building and make the necessary tools, but we have accomplished it, and if British users could be induced to visit us and see what we have done and what it has involved, we should be very pleased.

Mr. Perkins: I was struck by the remark of Professor Desch in his paper when he said that microscopes wear because of the bad material of racks and pinions. I have found in a fairly long experience of microscope repair that sometimes the German slides are softer than the English slides, so that does not, in my opinion, account for the fact that the English microscope wears quicker than the German. It has always seemed to me that the English makers, in spite of their undoubted ability, overlook the fact that if you want to reduce wear on the slides of a microscope, they must bear properly upon each other. It is no good putting in slides which bear at points, as in Fig. 1. Wear very quickly takes place at those points and develops a shake, and you get a loss of stability, such as Professor Barnard spoke of. The closest analogy I can put forward is an ordinary bearing. If, for argument's sake, the inner bearing is much smaller than the outer (Fig. 2), you get point metal to metal contact and quick wear. If, however, it fits as in Fig. 3, the lubricant stops in in an unbroken film, and you get long and efficient wear. I have seen microscopes 20 years old which have no shake in them and still fit perfectly all over. Then, again, the weakness of design of the usual spring fitting is another point which

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in my opinion English manufacturers have always overlooked. If you spring at four corners, like *a*, *b*, *c*, *d* (Fig. 4), the fitting E has got to be a very fine fit, and also the fitting F, but directly you start springing E you distort F at once. I have seen it; I have spent hours over it worrying about it, but English makers are

FIG. 1.

FIG. 2.

FIG. 3.

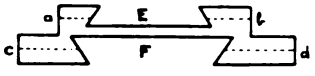

FIG. 4.

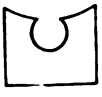

FIG 5.

gradually waking up to the fact that you have got to have your slides in a springless chunk of metal, something like that shown in Fig. 5, so that when you do the screws up, the chunk of metal remains as it was and does not distort. Again, how can you efficiently remove the grinding material from the springing slots, which is another obvious source of wear.

Mr. Beck: Was the microscope 20 years old which you referred to German or English?

Mr. Perkins: It was German. I am not saying that I have not seen an equally good English instrument 20 years old, but I am speaking of English instruments as a body. Another point is that English makers must now see to it that they have an efficient system of inspection. The Germans have a very efficient system of inspection, and English makers must see that nothing leaves their factories which is not perfect. When you have got to that point, but not before, then success is assured.

Mr. Harold Wrighton: It fell to my lot to prepare the photomicrographs which were shown in the paper given by Sir Robert Hadfield and Mr. T. G. Elliot at the Symposium. These photographs were taken on a Zeiss-Martens horizontal machine. In order to obtain them I found it necessary to alter radically the long distance fine focussing adjustment. Even in the best patterns of photomicrographic apparatus the design and efficiency of this long distance focussing fittings seems to receive very little attention. Possibly a description of the new arrangement may be of interest to some gentlemen who have a similar Zeiss-Martens outfit.

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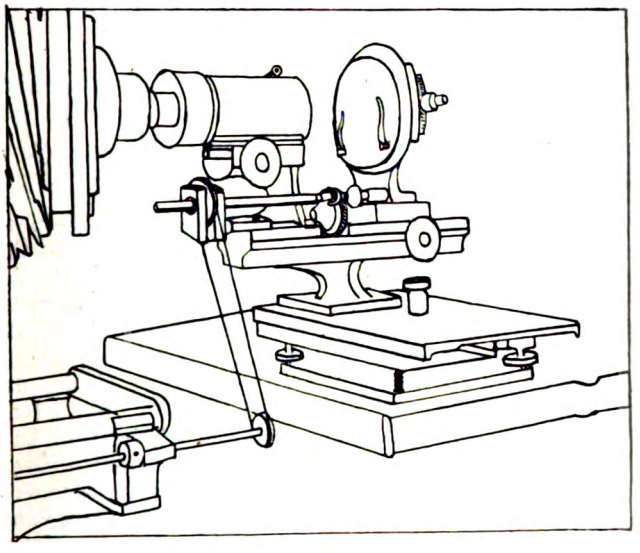
The arrangement shown in the accompanying sketch was made in the works at very small cost, and has proved very satisfactory. The short metal rod which fitted into the socket on the focussing rod has been replaced by a longer rod, $\frac{1}{4}$ in. square in cross section. A $1\frac{1}{2}$ in. pulley wheel, turning on flanges, is mounted on a bracket at the corner of the microscope base. A square hole through the pulley wheel is just large enough to allow of very slight play between the wheel and the square rod. As the square rod will pass along through the pulley wheel, horizontal traverse of the microscope stage is not interfered with. A long rod is mounted in brackets screwed



to the base, which carries the camera. This rod has a $\frac{3}{4}$ in. pulley wheel at one end, which is connected by cord to the other wheel. At the other end is a 2 in. milled brass head, for turning. The two grooved wheels over which the cord passes are milled inside the grooves, thereby preventing slip. The arrangement as made to dimensions given above further reduces the speed of fine adjustment by one half. The main advantage is that, owing to slight play between wheel and square rod, any slight torsion produced whilst turning the rod can ease itself when the hand is removed, without turning the fine adjustment and disturbing the focus.

Another matter, referred to by a previous speaker, is the lack of contrast in most metallurgical specimens as compared with a biological section. This is one of our difficulties, and, as a matter of fact, most of our photomicrographs show considerably more contrast than is actually present in the specimen.

Mr. T. Smith: I would like to have spoken on the optical side of the discussion, but there is one matter I will refer to. We have been given some figures by Commander Ainslie based on a displacement of 1/100 mm., and some further results on a basis of the same magnitude, with the displacement along the axis, may be of interest.

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I have worked out some figures relating to a 2 mm. objective. N.A. = 1.4, which gives perfect definition when used properly. With the object displaced 1/100 mm. from its proper position, I find that the marginal rays, instead of converging to the paraxial image point, get farther and farther away from the axis. This indicates how accurately it is necessary to focus at high magnifications. Therefore I would like to suggest that manufacturers of apparatus for high power work and particularly for ultra-violet microscopy should pay special attention to the problem of adjusting the specimen accurately in relation to the objective. Particularly when short wave-lengths are being used, as in ultra-violet microscopy, is this necessary if much time is not to be wasted in taking useless photographs.

The Chairman: We now proceed to the discussion of the OPTICS OF THE MICROSCOPE, and I will ask MR. WHIPPLE, President of the Optical Society, to take the Chair.

Mr. R. S. Whipple: I think that at this stage of the proceedings we ought to congratulate Messrs. Beck on the fact that they have been able to produce a standard microscope and that they have been able to keep their promise to produce it this month. As a manufacturer I know the difficulty of keeping a promise of this kind, and it is greatly to their credit that they have been able to keep to time. As a manufacturer, I also know some of the difficulties involved in the production of a new instrument. They have covered the foot of the stand with ebonite. To do this is in itself an achievement; they have introduced this ingenious geometric arrangement for holding the objectives, another considerable achievement. Thus in this apparently simple looking article there are a number of mechanical achievements—I venture to say great achievements—which a few years ago would have been regarded as impossible. I think, therefore, that it is not right to pass from the mechanical side of the microscope without expressing our indebtedness to them for what they have done so far, and to wish them and other English microscope makers every success in the future.

Abstracts of the following papers were then presented:—

THE OPTICS OF THE MICROSCOPE.

PROFESSOR A. E. CONRADY, "Microscopical Optics."

DR. H. HARTRIDGE, M.A., "An Accurate Method of Objective Testing."

MR. H. S. RYLAND, "The Manufacture and Testing of Microscope Objectives."

MR. F. TWYMAN, "Interferometric Methods."

DISCUSSION.

Mr. Conrad Beck: I have been greatly interested in the Hartridge test for microscope object glasses. Whether the graphs that you get are any value or not, it is impossible to say. I should not at present like to express the slightest opinion; all I can say is that I was interested to find that the graphs which we took in succession

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one after the other with the same object glass were fairly consistent, which, considering the conditions under which these observations are made, is rather remarkable, because one is using an extremely small portion of the object glass at one time. The principle is that by the use of a small diaphragm you are illuminating a small zone of the object glass, and the numerical aperture of the portion you are illuminating is very small. I did not expect that our results would agree, because of the extremely inferior image produced with such a small portion of the object glass being used at one time. In discussing this matter with Dr. Hartridge, he pointed out that his microscope was not nearly sufficiently rigid for the purpose. The matter has been considered by my firm, and they came to the conclusion that there was no microscope sufficiently rigid for the purpose, and consequently for the last eight weeks we have been designing an instrument which I am proposing to make for my own personal use that I hope and think will be the most perfect microscope stand ever made. I shall show it to the Society as soon as it is made. Those who use the microscope for general work may consider it too elaborate and expensive for ordinary purposes, but I am not sure. It will have some features about it that will make it unusually rigid. Its construction is an interesting engineering problem, and whether anybody will ever order a similar one may be doubtful, because the cost will be very great.

There is one point made by Dr. Hartridge in his paper which I think is an obvious error, and if it were pointed out I think he would admit it. The method of testing the object glass is only a test to see whether the light from a lens is going to one point. It is not a test of the sine condition. That must be carried out as a separate test, and I am bound to say that my own impression is that when the Hartridge test is worked out and his method of calibrating and plotting out has been done, we shall find we are testing an important, but not by any means the most important, correction on an object glass. The important points about an object glass, apart from achromatic corrections, are firstly, that the light from the whole object glass shall go on to a point, and secondly, that the focal length of every zone in the glass shall be the same, and it is this latter point that the sine condition guarantees. Mr. Hartridge's test has some analogy to the Hartmann test; it measures the lateral shift of the uncorrected rays instead of the longitudinal error.

Commander M. A. Ainslie, R.N.: I should like to concentrate attention on the subject of the condenser. Professor Conrady refers to the incorrect position of the iris diaphragm; this is certainly most marked, but there are one or two points to be considered in this connection. There is no reason why the iris diaphragm should not be placed between the top lens of the condenser and the next lens, or perhaps a little lower down; at any rate, much higher up that it is at present. The diaphragm could be very well worked by means of a bevel wheel and a pinion coming out radially; the only thing against this is that the stage is so thick. It would be quite impossible on the standard instrument here shown, but if we were to return to the "horseshoe" type of stage designed by Nelson, it could be done perfectly easily. Presumably, however, the exit pupil of the objective is in the neighbourhood of its upper focal

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plane; as a general rule I fancy it is rather lower down, but the position does not seem to be constant, even in objectives of the same type. If the obliquity of illumination at the margin of the field mentioned by Professor Conrady is to be avoided, the iris will have to be in the back focal plane of the condenser; if that is the case, no lateral movement of the condenser will affect the position of the image of the iris-aperture in the back lens of the objective, and it will be impossible to judge of the centering by looking down the tube.

Again, I think that both opticians and users of the microscope are content with too little in connection with the performance of the condenser; and I should say that the objection that the slide is composed of "window glass" introduces another "bogey." The area involved is always small, and if an oil immersion condenser is used, the surfaces of the slip cease to exist optically. At any rate, with a first rate modern achromatic condenser, such as the Watson "Parachromatic," it is possible, when the light source has a screen extending half way across it, to focus with such sharpness an image of the edge of this screen on the object that one row of dots on, say, *Pleurosigma Angulatum* shall be in full light and the next in "full darkness"—and this with an N.A. in use of not less than 0.7. This means that it is possible to get sharpness of the order of $\frac{1}{50.000}$ of an inch. But this is only done on one condition, and that is that the distance of the light-source is carefully adjusted to the thickness of the slip; as carefully as we adjust tube-length to the thickness of the cover glass. This point is almost universally avoided by the text-books, and I want to bring it forward as strongly as possible.

Mr. T. Smith: With regard to increasing the resolving power of microscope objectives, there is little doubt that the numerical aperture, as it is ordinarily understood, can hardly be increased with advantage, but there is considerable prospect of obtaining increased resolving power by using shorter wave-lengths of light. There are very considerable difficulties at present in the way, but I see no reason why they should not be overcome, although an extraordinary amount of experimental work will be involved. It is necessary to know the properties for such light of a very great variety of materials. Where we already possess some knowledge of the behaviour of certain materials with regard to ultra-violet light, this information must become much more precise than at present before it can be considered adequate, and I should like to see some definite encouragement given to researches of this character, because they can hardly fail to lead to results of value to the microscope user. Coming now to objectives and their design, it seems to me that this subject has never been investigated systematically, but that new objectives have generally been a further development of old designs on known lines. I should like to see systematic investigations undertaken, so that we may know what prospect there is of effecting real improvements in the corrections. For example, in a high power objective we have a lot of lenses placed very close together, though I am not aware of any thorough investigation which justifies adherence to this arrangement. There are obvious difficulties in the way of large separations; nevertheless, there would appear to be some decided advantages to

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be gained. At present with apochromatic lenses the curvature of the field is due to the properties of the transparent materials we employ. In general they have very similar properties as regards relative dispersion, and this imposes very severe limitations on what can be achieved; but these limitations no longer hold if the lenses are well separated, and it is possible that material improvements may be effected by radical alterations in the type of objective. There would be difficulties in doing this with objectives for ordinary use, but they would hardly apply at all for a special instrument required to give very great magnification, such as the metallurgists ask for, and I think these investigations might very well be made in regard to objectives for this particular purpose. In fact, I think we want to see a very great deal more of the design and manufacture of objectives for special purposes instead of expecting one objective of a given focal length to do any and every job. It ought to be realised more generally that an objective of high resolving power differs markedly from a so-called universal objective like a photographic anastigmat. A microscope objective of large N.A. is necessarily a very poor instrument for any conditions but precisely those for which it is designed. There are many other points to which attention might be called, but it must suffice now to mention one. A great deal has been said about the variation in the definition given by similar objectives made by the same firm from similar glass, which ought therefore to be identical in performance. I want to suggest that a possible contributory cause may be insufficiently accurate centering of the surfaces. I do not think that investigations have ever been carried out on methods of getting surfaces centered to an extraordinary degree of accuracy, yet a very high degree of accuracy is obviously required in a microscope objective. I have seen photographic lenses under examination with the interferometer, and these have shown marked irregularities in the wave front towards the periphery of the lens. When we seek the highest possible resolving power, it is the periphery of the lens that is all important, so I think we want to see, among other things, an investigation into methods of getting surfaces centered, not twice as accurately as we do them at present, but perhaps 10 or even 100 times as well. If any manufacturer were able to effect such an improvement, he would probably find that his lenses would realise a much more uniform standard of excellence than those produced at the present time. I very much hope that in some of the directions I have indicated the National Physical Laboratory may be able to give assistance to our own manufacturers.

Mr. J. E. Barnard: Mr. Smith has just referred to the question of investigation by the use of radiations of short wave-length. I should have hesitated to bring the subject up again had it not been that Professor Conrady also referred to it in his paper, and by a curious chance he has dropped into a not unusual error. He says that the limitations of the work are in part laid down by the opacity of bodies to ultra-violet light. When you get down to the dimensions with which we are dealing in a microscopic object which is at or beyond the ordinary resolution limits, opacity is almost non-existent. Sir George Beilby has shown that very thin metal films

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are almost perfectly transparent, and yet metals are the most opaque of substances. Latterly I have been endeavouring to photograph by means of ultra-violet light some exceedingly small organisms, some of which are beyond the limits of resolution, and the difficulty has been that with any wave-length I have at present available, the organism is transparent. The radiations pass completely through, and I am unable to get an image of any description whatever. So that to say that the limitations of the work are largely governed by the opacity of small bodies is not in accordance with practical experience or theoretical expectations. It may possibly arise if we use radiations of much shorter wave-length than those at present available, but in that case we shall be working with a microscope *in vacuo*, and I do not think it is a point which is likely to arise in practice for some time to come, although it may, and probably will, arise at a later stage.

Mr. L. C. Martin: I was interested in the description of the Hartridge test for the microscope objective, but I should like to say that it is not often, I believe, that a man testing a microscope objective wishes to know the aberration to any great accuracy, but rather whether the microscope objective is sufficiently good for the purpose. Therefore a somewhat easier quantitative test is to be desired. At the present time I have been doing a certain amount of work as a sort of preliminary study of the star test, and I think that possibly the so-called Rayleigh condition of less than one quarter wave-length a speedy test of the aberrations of a microscope objective.

Professor Conrady remarks in his paper that the fulfilment of the so-called Rayleigh condition of less than one quarter wave-length difference of optical paths between paraxial and marginal rays in good telescope and microscope objective, has been demonstrated by the Hilger interferometer. It is easy to understand that, imagining a perfectly spherical mirror in the interferometer and a means of controlling the position of such a surface to correspond with any particular focus of the test lens, such a perfect demonstration could be given. It is not easy to understand, however, when we consider that the errors of the surface of a mirror, which may be of the order of $\frac{\lambda}{4}$ or even more, are doubly important in such a case, and that the position of the test focus has to be obtained by trial. It is only when we consider a fact which was hinted at by Lord Rayleigh in 1879, and worked out by Professor Conrady in his paper on Star Discs, viz., that the effects of spherical aberration can often be countered very completely by changes of focus (or in mathematical language that we can partly balance the terms of the fourth and higher orders in the aberration expression by a change of the coefficient of the second order), that we can realise that the indications of the interferometer are trustworthy even to the extent previously indicated. It is necessary to bear in mind, however, that there is nothing magically sensitive in the interferometer tests as compared with star tests, for example, if these are performed with the maximum of care. Those who expect them to give tremendously sensitive results far excelling all other tests are doomed to disappointment.

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Mr. Beck: Will you explain to us whether a quantitative measurement is obtained in the star test. The star test has been in use with the microscope objective ever since the achromatic microscope objective was known, in the form of a minute mercury globule reflecting a small source of light which makes practically an artificial star.

Mr. Martin: The work I have been doing is in a very unadvanced stage, but I hope it will be possible to obtain a rough estimate of the variation of the spherical aberration.

Commander Ainslie: I had the curiosity to test a low power objective on the well-known Wassel method, and it was easy to obtain (by this particular method of the extinction of the two sides of a zone simultaneously, with a screen), numerical values for the different foci of the different zones. I was only using a low power objective, an half-inch apochromat, and it would be difficult with high powers, unless, perhaps, an auxiliary telescope is used.

Mr. T. Smith: Mr. Beck said that the Hartridge test would not give coma. May I suggest that it is quite easy to get coma by plotting the spherical aberration for two somewhat different magnifications. From these numerical values, the deduction of the coma is quite easy.

Professor Eyre, in bringing the discussion to a close, said :

The time has now come when I must close the meeting. It is very difficult at the end of an evening o this character to sum up with anything like precision or to offer an opinion that has any value on the work that has been presented. There is, however, one outstanding feature, namely, that workers are willing and anxious to state their requirements to the manufacturers, and I think we have evidence that the manufacturers on their side are willing to do all in their power to help meet these needs. We cannot expect perfection at once. As Mr. Watson Baker has said, it has taken quite a year to get his factory and the machinery ready. It has been the same with all manufacturers and I do trust now that the necessities of the workers have been placed clearly before the manufacturers that we shall soon reach a stage when we shall have an instrument of our own manufacture, not only for home use, but one which will also enable us to capture the world's trade in microscopes.

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APPENDIX I.

Catalogue of Exhibition,

Held in connection with

THE SYMPOSIUM AND GENERAL DISCUSSION

ON

The Microscope: Its Design, Construction and Applications,

On Wednesday, January 14th, 1920, in the Rooms of the Royal Society, Burlington House, Piccadilly, W.1.

GROUND FLOOR.

A SELECTION OF MICROSCOPES FROM THE COLLECTION IN THE SCIENCE MUSEUM, SOUTH KENSINGTON.

Lent by the Board of Education.

The instruments selected are arranged in chronological order, and illustrate the development of the compound microscope from the end of the sixteenth century until towards the middle of the nineteenth century.

Jansen's microscope (1590) is represented by a facsimile copy, and Hooke's microscope (1665) by a photograph of the Plate in his "Micrographia."

The rest are chiefly examples of the work of the leading English opticians of the eighteenth and early nineteenth centuries, viz., Marshall, Culpeper, Cuff, Martin, Adams, Mann, Watkins, Bleuler, Dollond, Smith, Ross, Powell, Tulley, and Pritchard.

To mark the introduction of the apochromatic objective a microscope by Zeiss, made in 1888, is also shown.

These instruments, which are not the property of the Board, are exhibited by permission of the owners, Mr. Thomas H. Court and Mr. Edward M. Nelson.

Descriptive labels are shown with the instruments.

LIBRARY.

(*First Floor.*)

MR. CHARLES BAKER.—Demonstration of photomicrographic apparatus, equipped for metallurgical research work, ultra-condenser, concentric dark ground illuminator, and recent introductions of new microscopes and objectives.

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MR. A. C. BANFIELD.—Thirty glass transparencies illustrating the application of the microscope to low power stereoscopy. The subjects shown range in magnification from four diameters to seventy.

MR. J. E. BARNARD and MR. F. WELCH.—Quartz and glass mercury vapour lamps as illuminants for the microscope.

PROFESSOR W. M. BAYLISS, F.R.S.—

(a) Ultra-microscope of Siedentopf-Zsigmondy pattern, showing Brownian movement in colloidal gold.

(b) Heating chamber for use with "cardioid" condenser, showing cessation of Brownian movement on gelatin.

MESSRS. R. AND J. BECK, LTD.—The Beck Standard London Microscope to specification of the British Science Guild. Sloan object changer. High-power dark ground illuminator. Beck micrometer eye-piece.

MESSRS. BELLINGHAM AND STANLEY, LTD.—Instruments for measuring refractive indices.

Improved Abbe refractometer; all British design, enables refractive indices of solids or liquids to be determined at average accuracy of two units in the fourth place. The partial dispersion C—F can also be measured. The immersion refractometer shown is identical in principle, but is designed for use with liquids, being suitable for alcohol determinations. Refractive index plays an important part in microscopy, not only for materials used in objectives, but also in the case of various mounting media.

MESSRS. BOOTS' PURE DRUG COMPANY, LTD.—The use of the microscope in pharmacy and pharmaceutical chemistry.

MESSRS. BRITISH COLLOIDS, LTD.—Colloidal suspensions under dark-ground illumination, to show Brownian movement.

MESSRS. BRITISH DYESTUFFS CORPORATION (HUDDERSFIELD), LTD.—Dyestuffs used for staining.

Basic Colours:—
Auramine O.
Bismarck Brown R.100.
Magenta Crystals.
Malachite Green Crystals A 25 per cent.
Methyl Violet 2B.
Methylene Blue 2B.

Acid Colours:—
Nigrosine G. Crystals.
Orange G.

MESSRS. THE CAMBRIDGE AND PAUL INSTRUMENT COMPANY, LTD.—Reading microscope. Microscope used in the accurate cutting of screw threads. Microtomes.

MESSRS. CHANCE BROS. AND COMPANY, LTD. (MR. F. E. LAMPLOUGH).—Optical glass.

MR. A. CHASTON CHAPMAN, F.I.C.—Some cultivated and "wild" yeasts in pure culture; the former are used for brewing and distilling purposes; some of the latter are frequently a source of trouble in the brewery.

MESSRS. CO-OPERATIVE WHOLESALE SOCIETY, LTD. (DR. GEOFFREY MARTIN, F.I.C.).—The use of the microscope in the preparation of foodstuffs.

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MESSRS. COURTAULDS, LTD.—The use of the microscope in the textile industry.

Exhibit A.—Samples of artificial silk and cloth, and microscope with sample of cloth under low power, illustrating employment for studying character of textiles.

Exhibit B.—Microscope with sample of natural souple silk stained blue, illustrating identification of fibres.

Exhibit C.—Microscope with cross-sections of modern viscose artificial silk, and photomicrographs showing differences in cross-sections of typical artificial silks, illustrating identification of origin and method of manufacture.

MESSRS. F. DAVIDSON AND COMPANY.—The "Davon" patent super-microscope and optical bench for direct visual observations under high power, large field and great "depth of focus," and embodying a new method of photomicrography.

MR. D. FINLAYSON, F.L.S., AND MR. RAYMOND FINLAYSON, F.R.M.S., F.Z.S.—The microscope and its uses in seed analysis. Identification and comparison of different species of seeds and their adulterants, by means of a revolving disc attachment to stage of microscope.

THE GEOLOGICAL SURVEY AND MUSEUM (SIR AUBREY STRAHAN, F.R.S.).—A series of photomicrographs to illustrate the mineralogical constitution and structure of rocks as revealed by the petrological microscope, and specimens to illustrate the mode of preparation of thin rock-sections for microscopical examination.

LIEUT.-COL. WILLIAM GIFFORD.—Monochromatic light filters for use in high-power microscopy and photomicrography. F line for visual work, G for photography.

MESSRS. FLATTERS AND GARNETT, LTD.—Photographs of textile fabrics and fibres.

MR. J. W. GORDON.—Demonstration of the principles of illumination in the microscope, with special reference to:—

1. Wide-angled lighting.
2. Narrow-angled lighting.
3. Wide-angled vision.
4. Narrow-angled vision.

MESSRS. HADFIELDS, LTD.—Photomicrographs of iron and steel.

MR. R. J. E. HANSON, F.R.C.S.—

Dyoptikon (Eye-piece) Headrest.

[Applicable to any existing standard microscope.]

A sliding headrest is provided, with rubber tubular buffer—to lessen fatigue and mal-orientation of the eyes and to secure effective retinal adaptation and stimulation of (R and L) visual cortex.

A Solution of Visual Purple.

DR. H. HARTRIDGE.—

(1) Apertometry by means of the descending light-path.

(2) Water-soluble immersion medium for use with high-power objectives.

(3) Critical illumination with immersion condenser, the light source being attached to and forming part of the microscope.

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DR. W. H. HATFIELD.—Photomicrographs illustrating application of microscope to metallurgical work.

MR. E. HATSCHEK.—Ultra-filters for retaining ultra-microscopic particles. Collodion membrances are used as septa: according to the method of preparation they may be used with pressure (Bechhold) or they may work with hydrostatic head only (Wo. Ostwald).

MESSRS. HAWKSLEY AND SONS.—Microscopes by the Spencer Lens Company suitable for research work, students' models, also travelling model in all-metal case. Blood examination apparatus. Thoma-Hawksley haemacytometers with various rulings.

MR. C. F. HILL AND MR. H. C. LANCASTER.—The use of the microscope in the metallography of lead. Typical samples of lead, containing antimony, tin, copper, and zinc. Also a new bearing metal, made of lead, containing calcium and barium.

MISS NINA HOSALI.—Models illustrating crystalline form and symmetry.

MESSS. ILFORD, LTD. (MR. F. F. RENWICK).—Exhibit arranged to show the range and spectrum of thirty colour filters, including a set of nine micro-filters, eight spectrum (single-band) filters, tri-colour filters and their complementaries, mercury vapour lamp filters and photographic correction filters.

JAEGER LABORATORY (MR. A. E. GARRETT).—

Exhibit Illustrating the Analysis of Textiles.

The microscope is the final Court of Appeal in the testing of textile materials in so far as the nature of their constituent fibres is concerned.

There is no difficulty in dividing the more generally used fibres into the following distinct classes:—

1. Wool and other animal hairs.
2. Silk.
3. Cotton.
4. Other plant fibres (flax, ramie, jute, etc.).

Classes 1 and 4 are, however, as indicated, subject to much subdivision.

Class 1 contains wool, camel hair, alpaca, vicuna, cashmere, mohair, and a few less well-known hairs. Class 4 contains all the multi-cellular fibres obtained from the stems or leaves of plants, and their number mounts up considerably, especially if those employed for sacking, rope, etc., are included.

The distinguishing features in Class 1 are the diameter of the fibres, the colour of the pigment when present, the distribution of the pigment cells, and scale structure or other surface markings.

In Class 4 the diameter of the fibres, the nature of the cell walls—uniform thickness, etc.—the size of the lumen, and superficial markings help in the recognition of the fibre. Polarised light will often assist in this section.

The microscope can also be used to determine:—

(a) Whether the fibres are in their normal state or have undergone treatment which has altered their shape. Mercerised cotton is a good example.

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(b) Whether coloured fibres owe their tint to natural pigment or dye. The pigment cells appear as separate units, while the dyed fibres appear of uniform tint throughout.

MESSRS. JEYES' SANITARY COMPOUNDS COMPANY, LTD. (MR. W. C. REYNOLDS, F.I.C.).—Illustrating the theory of emulsions.

MESSRS. KODAK, LTD.—Filters for photomicrography, spectroscopy, tri-colour photography, filter-holders and other photomicrographical accessories, plates for photomicrography.

THE PHOTOMICROGRAPHIC SOCIETY.—

MR. F. MARTIN DUNCAN, F.R.M.S., F.R.P.S., F.Z.S.—Prints of low and high power photomicrographs, including bacteria, etc.

DR. G. H. RODMAN, F.R.P.S.—Transparencies of photomicrographs of a variety of subjects, in viewing frame.

MR. E. A. PINCHIN, F.R.M.S.—Transparencies of photomicrographs of diatoms, in viewing frame.

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Features:—

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(b) Modified objectives (converted to short barrel from standard lenses).

(c) Half-watt lamp, affording sufficient illumination at minimum expense and trouble.

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MR. SYDNEY W. ROSS, F.R.M.S.—A new apparatus for the microscopic examination and photomicrography of metallic specimens (two forms, drawings only).

RESEARCH DEPARTMENT, WOOLWICH.——

(1) Microscope with filar micrometer eye-piece, used for the measurement of small Brinell ball hardness impressions (0.2 to 0.8 millimetre in diameter) to 0.001 millimetre.

(2) Photomicrographs of structures found in gun-steel, shell-steel, etc.

M. EUGENE SCHNEIDER AND M. CHARLES FLORIAN.—A microscope for measuring Brinell depressions. (Constructed by the Société d'Optique et de Mécanique de Haute Precision, Paris.)

SHEFFIELD UNIVERSITY, by kind permission of the Vice-Chancellor, Sir W. H. Hadow (Professor W. Ripper, and Dr. J. O. Arnold, F.R.S.).

Original Specimens Belonging to Sorby.

(1) The following is a description of the Sorby micro-sections:—

Dr. H. C. Sorby's pioneer micro-sections of iron and steel, made in 1863-5.

Lent in 1889, for Dr. Sorby's lifetime, to Professor J. O. Arnold, F.R.S., and bequeathed on Dr. Sorby's

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death in 1908 to the Metallurgical Department of the University of Sheffield.

(Prepared by Dr. H. C. Sorby, F.R.S., at "Broomfield," Sheffield, 1863-5.)

(2) The gold copper series of micro-sections prepared by Professor J. O. Arnold, F.R.S.:—

Pioneer sections made by Professor J. O. Arnold, F.R.S., and Mr. Joseph Jefferson in 1893, showing the micrographic influence of small amounts of impurities on the structure of pure gold and copper, hence the discovery of brittle intercrystalline cements.

These were fully described in *Engineering*, February 7th, 1896.

(3) Framed signed portrait of the late Dr. H. C. Sorby, F.R.S.

Professor Alexander Silverman (University of Pittsburgh).—A new illuminator for opaque objects. (Exhibited by Mr. S. C. Akehurst.)

Dr. J. E. Stead, F.R.S.—An improved form of workshop microscope designed by Dr. J. E. Stead and Messrs. J. Swift and Son.

Series of heat-tinted specimens, showing the structure of phosphoretic steels and metals.

Dr. Marie Stopes.—The microscope as applied to coal research. Illustrated by thin sections of coal, showing differences in texture and of plant content.

Mr. J. Strachan.—The use of the microscope in the examination of paper-making materials.

(1) A series of slides showing various paper-making fibres, including both those in common use and a few unusual fibres used during the war.

(2) A series of slides showing dendritic growths of copper compound in paper, illustrating the application of the microscope to the study of chemical changes taking place in paper after its manufacture.

Messrs. James Swift and Son, Ltd.—Microscopes for metallurgy and mineralogy and apochromatic objectives.

Messrs. Taylor, Taylor and Hobson, Ltd.—

A microscope for measuring the diameters of depressions made when testing the hardness of metals by the Brinell method.

The magnification is 16 diameters.

A graticule is incorporated enabling diameters up to about 7 mm. to be measured.

The microscope stands on three feet, one of them being a cloven foot, within the notch of which the object is easily centred in the field of the microscope. The other two feet are adjustable up and down by means of a knurled nut.

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The optical system is contained in a single tube, and may be removed as a separate unit. The field and object glasses and the graticule are held in the tube by a novel and very simple means (patented) without screws.

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APPENDIX II.

THE WORK OF THE FARADAY SOCIETY,

And a brief reference to Michael Faraday,

BY THE PRESIDENT OF THE FARADAY SOCIETY

(SIR ROBERT HADFIELD, Bart., D.Sc., D.Met., F.R.S.)

As in addition to our own Members, we have a large number of visitors present to-day, I thought it would be of interest to write a short account of the work of our Society, which takes its name from one of the greatest of the Scientific Immortals—Michael Faraday. I need hardly say how glad we shall be to receive an access to our Membership of those interested in the work we are trying to accomplish, which is not only that of covering certain ground not dealt with by other Scientific Societies, but also of arousing interest in the minds of the younger men in our great Metropolis and elsewhere with regard to Scientific developments.

I also take this opportunity of saying a few words about Faraday, who devoted his life to Science, with but one single aim—to advance its position in the world, and to benefit Mankind without fear or favour to rich and poor alike. No monetary or selfish considerations ever entered his mind.

At the time I accepted the invitation of the Council in 1914, conveyed through my friend, Professor A. K. Huntington, to be your President, I was not in good health, and the duties seemed to be far too great for me to undertake. I felt, however, that it was a special honour and privilege to be asked to follow in the footsteps of some of our great Masters of the Past—Kelvin, Swan, and others—so I accepted.

When delivering my Presidential Address in June, 1914, I little dreamt that our Empire was so soon to pass through a time of unexampled stress. Notwithstanding the difficulties with which those five troublous years were surrounded, I am glad to say our work never relaxed, and I do not think we suspended a single meeting, Council, Committee, or General. Thanks to the willing help given on all hands, whether by the Council, by the Members, or by our Secretary, Mr. F. S. Spiers, it has given me no little satisfaction to think that the younger men amongst us have been aided in their work by our Society and its gatherings.

My work with the Faraday Society has been a labour of love. The time is, however, coming when I am sure you must think it only right that another of your Members should take my place as President. Let me add that I have only been too glad to give any help in my power, and its future will always have the warmest interest of my heart.

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Our Society owed its origin in 1902, chiefly to a little band of workers who met together to advance the great cause of Scientific Knowledge. It was founded on February 4th, 1903 at a meeting in the rooms of the now defunct Faraday Club, held at St. Ermin's Hotel, Westminster. Amongst its founders were Mr. Sherard Cowper-Coles, Mr. W. R. Cooper, Professor F. G. Donnan, Dr. F. M. Perkin, Mr. Alexander Siemens, Mr. James Swinburne, and Mr. F. S. Spiers, our present Secretary, to whom we owe a deep debt of gratitude for his indefatigable work on behalf of our Society, and to whom there should be accorded a crown of laurels. To each of these Founders I have sent a special invitation asking them to be present this evening.

Our first President was Sir Joseph Swan, F.R.S., later Lord Kelvin, followed by Sir William Perkin, F.R.S., Sir Oliver Lodge, F.R.S., Mr. J. Swinburne, F.R.S., and Sir R. T. Glazebrook, F.R.S., whose portraits are given in the accompanying plate. The objects of the Society as originally defined were to promote the study of Electrochemistry, Electrometallurgy, Physical Chemistry, Metallography, and kindred subjects.

I venture to think that we are accomplishing the objects for which its founders set out, and that the Faraday Society will continue to increase and flourish. It is, however, very desirable that we should extend our Membership, and I trust a great effort will be made by every present Member to bring in at least another new Member, also that many of our Visitors to-night will join our Roll Call. Stagnation in any Society means final decay. If we fulfil a useful purpose, as we undoubtedly do, then the aim I have set forth of a large increase in Membership ought to be possible. In one important Technical Society in America, I learn they have this year increased their Roll Call by no less than one thousand new Members.

Our Society is honoured and recognised in the Councils of the larger and parent Societies. It has a seat on the Conjoint Board of Scientific Societies and is consulted along with other Societies on the special subjects with which we deal and are acquainted. The fact that the Royal Society has this evening granted us the privilege of holding our Symposium in its historic building also shows, I venture to think, that our work meets with the approval of this great parent body of Scientists.

Nitrogen Products Committee.—I will refer to one subject in which we gave a helping hand during the War—in fact it might be said that the Faraday Society originated this special Research in this Country, namely, that relating to Nitrogen Products, which mainly through our suggestion was taken up by the Munitions Inventions Board. My friend, Professor Huntington, of King's College, worked in season and out of season to get the Government Department concerned interested. He finally succeeded in persuading the Munitions Inventions Department to appoint a Special Nitrogen Products Committee, who in their turn were instrumental in establishing a Research Department. As Mr. H. W. Dickinson, Secretary of the M.I.D., points out, so much spade work was done by the Department with regard to this subject that

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when at a later date owing to the submarine campaign the policy of the Ministry changed and it was decided to go to new sources for Nitrogen supply, the results of the research work and of the information gathered by the Research Department mentioned were ready to hand and enabled practical work on a large experimental scale to be commenced at once.

It should be added that the work was taken up for the Committee by one of our Members of Council, Dr. J. A. Harker, F.R.S., who was allowed by the National Physical Laboratory to assist in this important development, his labours being of the highest value. The Country is greatly indebted to him for the untiring devotion he has shown in working out this special and important subject to a successful issue. Our Council hope that before long they will be able to present a Report to us describing in detail the work carried out. The Report of the Committee itself is shortly to be published, and it will probably be one of the most remarkable documents in regard both to scope and matter that has been issued by a Government Department during those troublous times.

The work done, although not immediately made use of for War purposes, as the Armistice rendered any help needless in this quarter, will, without doubt, bear great fruit in the future; in fact, the Nitrogen Factory, which was being started during the War, has already been taken over by a private organisation. It is therefore probable that the Nitric Acid required in this Country for making explosives, dyes and drugs will be produced synthetically in this manner.

Symposia previously held.—Since the formation of the Faraday Society, we have had approximately 330 papers presented to us, most of them fully discussed. During my own term of office—1914 to 1919—some 180 papers have been read, and, including the present one, there have been fifteen Symposia held, attended by considerably over 3,000 Members and Visitors. The following shows these in tabular form:—

No.	Date.	Title.
1	Nov., 1914	The Hardening of Metals.
2	Oct., 1915	The Transformations of Pure Iron.
3	Dec., 1915	The Corrosion of Metals.
4	Mar., 1916	Methods and Appliances for the Attainment of High Temperatures in the Laboratory.
5	Nov., 1916	Refractory Materials.
6	Mar., 1917	The Training and Work of the Chemical Engineer.
7	May, 1917	Osmotic Pressure.
8	Nov., 1917	Pyrometers and Pyrometry.
9	Jan., 1918	The Setting of Cements and Plasters.
10	Feb., 1918	Electric Furnaces. (Symposium at Manchester.)
11	May, 1918	The Co-ordination of Scientific Publication.
12	Nov., 1918	The Occlusion of Gases by Metals.
13	Jan., 1919	The Present Position of the Theory of Ionisation.
14	April, 1919	Radiometallography.

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THE FARADAY SOCIETY

and six of its Past Presidents.

Sir JOSEPH SWAN
(First President)
1903–1904

Lord KELVIN
(Second President)
1905–1907

Sir WILLIAM PERKIN
1907–1908

MICHAEL FARADAY
1791–1867

Sir OLIVER LODGE
1908–1909

JAMES SWINBURNE
1910–1911

Sir RICHARD GLAZEBROOK
1912–1913

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It is hoped that the present Symposium will be no less successful than previous ones. Many Members and others at home and abroad have expressed their thanks for the useful work done by our Society. We have also tried to give a helping hand and encouragement to the younger men in our midst. This has been one of the chief objects we have always had specially in mind. Let our motto be "Thoroughness," and we shall continue to flourish and do still better work in the future.

The Work of Michael Faraday.—Turning now for a moment to Michael Faraday, from whom our Society takes its name, I will a little later on refer to one of the descriptions of the Great Scientist, by Professor John Tyndall, F.R.S., in his lecture before the Royal Institution in January, 1863, on "Faraday as a Discoverer."

De la Rive, the well-known French Scientist in his "Notice on Faraday's Life and Work," Archives des Sciences de la Bibliothèque Universelle, October, 1867, stated that the number of Faraday's Memoirs from 1820 to 1855, all of these important, was almost incredible.

Faraday was born at Newington Butts on the 22nd September, 1791, and finally passed away at Hampton Court on the 25th August, 1867.

Tyndall said that it seemed desirable to give the world some image of Michael Faraday as a scientific investigator and discoverer. He regarded the attempt to respond to this desire, whilst a labour of difficulty in adequately presenting a history of this great man, as also a labour of love. However well acquainted he might be with the researches and discoveries of the great master—however numerous the illustrations which occur to him of the loftiness of Faraday's character and the beauty of his life—still to grasp him and his researches as a whole; to seize upon the ideas which guided him and connect them; to gain entrance into that strong and active brain and read from it the riddle of the world—was a work not easy of performance. As he was a believer in the general truth of the doctrine of hereditary transmission, Tyndall, who shared the opinion of Carlyle that a really able man never proceeded from entirely stupid parents—said that he once used the privilege of his intimacy with Faraday to ask him whether his parents showed any signs of unusual ability. He could remember none. His father was a great sufferer during the later years of his life, and this might have masked whatever intellectual power he possessed. When thirteen years old, that is to say in 1804, Faraday was apprenticed to a book-binder in Blandford Street, Manchester Square; here he spent eight years of his life, after which he worked as a journeyman elsewhere.

Faraday was only 22 years of age when he obtained a position in the Royal Institution. His first contribution to Science appeared in the Journal of the Royal Institution in 1816, that is, in the publication known as the "Quarterly Journal of Science." I thought it might be of interest to give the following summaries by Tyndall of (1) Researches by Faraday, and (2) Discoveries by Faraday:—

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RESEARCHES BY FARADAY.

	PUBLISHED
First contribution to Science—Analysis of Caustic Lime from Tuscany	1816
Experiments on Sounding Flames	1818
Vaporisation of Mercury at Ordinary Temperatures	1821
On the Limits of Vaporisation	
Experiments on Alloys of Steel	
Vibrating Surfaces	1829
On the Quantitative Comparison of different forms of Electricity	1833
On the Absolute Quanti y of Electricity associated with the particles or Atoms of Matter	
The Power of Metals and other Solids to induce the combination of gaseous Bodies	
Extra Current—The influence by induction of an Electric Current upon itself	1835
On Frictional Electricity, Induction, Conduction, Specific Conductive Capacity, and Theory of Contiguous Particles	1835 to 1838
Further Researches on Liquefaction of Gases—Establishing the fact that Gases are vapours of Liquids possessing very low boiling points	1844
Speculations on the Nature of Matter and Lines of Force	1846
On the Diamagnetic Condition of Flame and Gases	1847
On Magne-Crystallic Action and Lines of Force	1848 to 1851
Magnetism of Gases	1850
Atmospheric Magnetism	
Electricity of Gymnotus	
Source of Power of the Hydro-Electric Machine	
Regelation	

DISCOVERIES BY FARADAY.

	PUBLISHED
Two new Compounds—Chlorine, Carbon and Iodine; Carbon and Hydrogen	1820
Alloys of Steel	1821
Magnetic Rotations	
Liquefaction of Gases	1823
Change of colour of Glass in Sunlight	1825
New Compounds of Hydrogen and Carbon	1826
Benzol	
Improvements in manufacture of Glass for Optical purposes. Afterwards the foundation of most important Discoveries, *e.g.*, Magnetisation of Light	1829
Peculiar class of optical deceptions—optical toy, the Chromotrope owed its origin to this	
Magneto-Electric Induction—Tyndall says: "Greatest experimental result ever obtained by an investigator. The 'Mont Blanc' of Faraday's achievements"	
Terrestrial Magneto-Electric Induction	
Identities of Electricities Static, Voltaic, Magneto, Thermo, etc.	1833
New Law of Electric Induction	
Laws of Electro-Chemical Decomposition—Definite Electro-Chemical Decomposition. Tyndall says: "This Law ranks in importance with that of the Definite Combining Proportions in Chemistry"	
Origin of Power in the Voltaic Pile	1834
Magnetisation of Light and the Illumination of the Lines of Magnetic Force. In other words, the Rotation of the Plane of Polarisation	1845
Diamagnetism or the Magnetic Condition of all Matter	
Atmospheric Magnetism	1850

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SUMMARY OF FARADAY'S WORK.

I will also quote Tyndall's Summary of Faraday's work somewhat fully as it is indeed worth reading. It is a stimulus to each of us according to his light to go and try to do likewise, even if in a smaller and humbler way.

Tyndall says:

"When from an Alpine height the eye of the climber ranges over the mountains, he finds that for the most part they resolve themselves into direct groups, each consisting of a dominant mass surrounded by peaks of lesser elevation. The power which lifted the mightier eminences, in nearly all cases, lifted others to an almost equal height. And so it is with the discoveries of Faraday. As a general rule, the dominant result does not stand alone, but forms the culminating point of a vast and varied mass of enquiry.

In this way, round about his great discovery of Magneto-Electric Induction, other weighty labours grouped themselves. His investigations on the Extra Current; on the Polar and other conditions of Diamagnetic Bodies; on Lines of Magnetic Force, their definite character and distribution; on the employment of the Induced Magneto-Electric Current as a measure and test of Magnetic Action; on the Repulsive Phenomena of the Magnetic Field, are all, notwithstanding the diversity of title, researches in the domain of Magneto-Electric Induction.

Faraday's second group of Researches and Discoveries embraced the chemical phenomena of the current. The dominant result here is the great Law of Definite Electro-Chemical Decomposition, around which are massed various Researches on Electro-Chemical Conduction, and on Electrolysis both with the Machine and with the Pile. To this group also belong his Analysis of the Contact Theory; his Inquiries as to the Source of Voltaic Electricity, and his final development of the Chemical Theory of the Voltaic Pile.

His third great discovery is the Magnetisation of Light, which may be likened to the Weisshorn among mountains—high, beautiful, and alone.

The dominant result of his fourth group of Researches is the discovery of Diamagnetism, announced in his Memoir as the Magnetic Condition of all Matter, round which are grouped his enquiries on the Magnetism of Flame and Gases; on Magne-Crystallic Action, and on Atmospheric Magnetism, in its relation to the annual and diurnal variation of the needle, the full significance of which is still to be shown.

These are Faraday's most massive discoveries, and upon them his fame must mainly rest. But even without them, sufficient would remain to secure for him a high and lasting scientific reputation. We should still have his Researches on the Liquefaction of Gases; on Frictional Electricity; on the Electricity of the Gymnotus; on the Source of Power in the Hydro-Electric Machine; on the Electro-

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Magnetic Rotations; on Regelation; all his more purely Chemical Researches, including his discovery of Benzol. Besides these he published a multitude of minor papers, most of which in the same way illustrate his genius."

Tyndall adds that no allusion is here made to his power as a Lecturer. Taking him all in all, it will be conceded that Michael Faraday was probably the greatest experimental Philosopher the world has ever seen. The progress of future research will tend not to dim or diminish, but to enhance and glorify the labours of this mighty investigator.

Speaking with regard to my own lines of research, as representing the Faculty of Metallurgy, I may mention that Faraday, in his experiments on Alloys of Iron with other Elements, in other words the production of Alloy Steel, carried out in 1821 and 1822, showed that a remarkable inspiration evidently existed in his mind as to the great future this line of research work presented. Singular to say it is just about 100 years ago that Faraday wrote several letters from the Royal Institution (in April and June, 1820), to his Swiss friend De la Rive, Professor of Chemistry, Geneva, in which he gave an account of some experiments on Steel made by himself and Stodart. The world's great technical advances during the last thirty years have been—and I say it unhesitatingly—in a large measure due to the introduction of Alloy Steels such as Faraday had in mind. As already mentioned, Faraday, with Stodart, started these researches at the Royal Institution, finally completing the experiments by sending his various mixtures to be melted at the Sanderson Works in Sheffield, this Firm being still in existence to-day. The specimens had to be sent by coach, the work being given to a trusty assistant who had to go down and see the experiments put in hand and completed. Beyond the work of Mushet this particular land of Research lay fallow for many years, in fact it was my own discovery and invention of Manganese Steel in 1882 which showed that the new world already indicated by Faraday was there ready to be explored. This exploration has rapidly taken place during the last thirty years, including the discovery and invention of Chromium Steel, Silicon Steel, Nickel Steel, Tungsten Steel, High-speed Tool Steel, Non-corroding, and many other types of Steels.

Almost as important was the fact that Alloy Steel necessitated special heat treatment, which again required and called for the use of scientific methods for the determination of temperatures, critical points, microstructure study, improved analytical methods, mechanical testing, hardness determination, observation of electrical conductivity, magnetic susceptibility, electrical resistance, hysteresis effects and other qualities.

In conclusion, this Society is indeed honoured in being allowed to bear the name of so great a man as Faraday, whose work is still benefiting our Empire.

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TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS.

Vol. XVI. Part 2. FEBRUARY, 1921. Price 15s.

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Chairman, Sir RICHARD GLAZEBROOK, K.C.B., F.R.S., President.

AN
ADDRESS
will be given by
Sir J. J. THOMSON, O.M., F.R.S.

The Right Hon. A. J. BALFOUR, O.M., F.R.S., expects to be present to extend a welcome to the Institute.

By order of the Board,

F. S. SPIERS,
Secretary.

10, Essex Street,
London, W.C.2.

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VOL. XVI. DECEMBER, 1920. PART 2.

BASIC SLAGS: THEIR PRODUCTION AND UTILISATION IN AGRICULTURE.

A GENERAL DISCUSSION.

At the Meeting of the Faraday Society held on Tuesday, March 23rd, 1920, in the Rooms of the Chemical Society, Burlington House, London, W., a GENERAL DISCUSSION took place on "BASIC SLAGS: THEIR PRODUCTION AND UTILISATION IN AGRICULTURE." **Professor F. G. Donnan, F.R.S., Vice-President**, presided over the Discussion.

Sir Robert Hadfield, Bart., F.R.S., President of the Society, who opened the proceedings, before inviting Professor Donnan to take the Chair made a Statement relative to the part the Faraday Society had taken in 1916 and 1917 in the initiation of the movement which led to the formation of the Nitrogen Products Committee of the Munitions Inventions Department, the Report of which was recently published. The Statement is printed in the Appendix, together with a copy of letters which had been received from the Ministry of Munitions.

The Chairman: The Members of the Faraday Society are very much indebted to Sir Robert Hadfield for pointing out how well we have done during the war. The Faraday Society certainly did very important service in directing the attention of the Government to synthetic nitrogen production, and had the war lasted another year,

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a very large factory or factories would have been built for that purpose; but, as it is, I may safely say without revealing any secrets, that very important things are going to happen in this country, all of which I think we owe to the stimulus of the Faraday Society. It is very appropriate that Sir Robert Hadfield should have referred to this question, because there is no more important subject in any country than the supply of a cheap and abundant supply of nitrogen fertilisers. These, together with other fertilisers such as phosphatic products and potash salts, are of vital importance.

We have a long list of papers, some of them by the most distinguished agricultural authorities in England, and I will begin by calling on **Dr. E. J. Russell** to open the Discussion, and give us a general survey of the subject.

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THE UTILISATION OF BASIC SLAG.

By E. J. Russell, D.Sc., F.R.S., Director of the Rothamsted Experimental Station.

The utilisation of basic slag in agriculture is one of those important developments in agricultural science for which the credit is due in the first instance to British investigators. The possibility of utilising basic slag was put to practical test by the late John Wrightson at Ferryhill and at Downton in 1884 and 1885, and, in spite of some opposition on theoretical grounds by other workers, a good case was made out. The first field experiments were carried out in the south of England, but the centre of interest soon shifted to the north, and the most striking tests were carried out at Cockle Park, under the direction successively of Professor Somerville, Sir T. H. Middleton, and Professor Gilchrist. To these three more than any others we owe the great advances in knowledge of the use of basic slag.

The standard experiments and the well known trials were all made with the Bessemer slag. If agriculturists could have been assured of a steady supply of, say, 300,000 or 400,000 tons per annum of high grade Bessemer slag containing some 20 per cent. of P_2O_5, there would have been no need for this discussion; the problem would have been the purely academic one of working out the constitution of the effective constituents of the slag.

The introduction of the basic open hearth process, however, has threatened the supersession of the Bessemer process, and agriculturists can no longer feel certain of receiving adequate supplies of slag of the type to which the old material belonged. Three distinct substances are now used under the one name of basic slag:—

(1) Bessemer slag, containing about 20 per cent. of P_2O_5 (43.6 per cent. tricalcic phosphate).

(2) Open hearth basic slag, 7 to 14 per cent. P_2O_5 (15.4 to 31 per cent. tricalcic phosphate).

(3) Open hearth basic slag, 7 to 10 per cent. P_2O_5 (15.4 to 21.8 per cent. tricalcic phosphate), in the manufacture of which a considerable proportion of calcium fluoride has been used.

The phosphorus of the first two types of slag is nearly all soluble (85 per cent. or more) in 2 per cent. citric acid under certain conventional conditions: that of the third type is not—only 20 per cent. or less dissolving.

It may be said at once that no important agricultural distinction between the first and second of these classes has been proved with certainty when the slags are used in quantities containing equal amounts of phosphorus, and so far as present information goes, these slags are of equal value per unit of phosphorus to agriculturists. There are, of course, disadvantages in low-grade materials, in that large bulks have to be handled, and therefore larger expenditure is

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incurred, and deliveries to the farm or field may be delayed. But when allowance has been made for these items, there is no great difference between the two classes of slag. The third class, however, is somewhat different, and agricultural investigators generally agree that it is less effective than the first two types, though they have not yet wholly succeeded in evaluating it.

Broadly speaking, the problem resolves itself into three broad divisions:—

(1) What is the agricultural value of the various basic slags likely to be available in the near future?

(2) Is this value related to the chemical constitution of the slag in any simple way that would allow of some chemical expression and on which an evaluation method might be based?

(3) Is it possible for the steel works to increase the phosphorus content of the slag and generally to increase the effectiveness of the so-called low-grade slags?

The determination of agricultural value requires in general two distinct types of experiments—pot experiments and field trials. Pot experiments are more accurate than field trials, being much more under control: results can be obtained in a single season which are reliable within about 5 per cent. On the other hand, the rigid control of the conditions introduces a large element of artificiality, so that the results are never final. In the writer's experience a positive result in pot experiments is not always paralleled by a positive result in the field, as some nullifying factor may come into operation; on the other hand, a negative result in pot experiments is usually associated with a negative result in the field.

Although the pot experiment gives useful information, the field experiment has always to be made before any idea can be formed as to the economic importance of the factor under investigation. It is necessary also that the field trial should be repeated on different types of soil and in different climatic conditions. Fortunately an organisation of agricultural investigators—the Agricultural Education Association—covers Great Britain, and enables co-operative trials to be made. An extended trial of the three types of basic slag is now being organised which should give much valuable information.

The difficulty of studying this particular problem in the past has been to obtain basic slag of known history. In one or two instances a long, laborious agricultural investigation has been deprived of much of its value because the slag supplied for the purpose was not what had been promised.

Field experiments when well carried out are liable to an error of about 10 per cent. Farmers' trials are less reliable: the error may be anything from 20 to 100 per cent., or even more.

Provided the supply of basic slag of known origin can be assured, the agricultural trials can be carried out by the sub-committee of the Agricultural Educational Association, which has been set up for this purpose.

So much for the method of investigation. We must now consider some of the general results. The old Bessemer slag has proved in the farmers' experience extraordinarily valuable for the improvement

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of heavy grassland: no single fertiliser has been anything like as effective for this particular purpose. The effect is mainly indirect, and is traceable to the remarkable development of white clover which follows the application of the slag. It is not yet ascertained whether this effect is due to direct action of phosphates on the plant, or whether the slag in some way is helpful to the micro-organisms associated with the clover root.

Whatever the cause, the result of this spread of white clover is to increase the stock of nitrogen in the soil, and add greatly to the soil fertility. Further, it adds considerably to the value of the herbage, clover being one of the best of the green foods available. Another factor also contributes to the nutritive effect: additions of phosphate to the soil tend to add to the phosphorus content of the crop, and this in turn raises its feeding value.

The use of Bessemer basic slag has not been restricted, however, to grassland. It has proved effective in increasing yields of crops on arable land, particularly in the West and North. So far as the evidence goes, the feeding value of the crop is also increased, though the experiments are not very numerous.

As already stated, the open hearth basic slag made without fluorspar has hitherto proved practically as effective as the old Bessemer slag when compared on the basis of equal amounts of phosphorus. The fluorspar slag, has, however, proved distinctly less effective in pot experiments and in Oldershaw's field experiments in Suffolk: it was also less effective (though quite good) in some of Robertson's field experiments in Essex. In the North and West, however, where the growing season is longer, it was nearly as good as the more soluble slag of the second type. We may infer that the fluorspar slag would probably be more effective in cool, moist regions than in hot, dry ones, though more information is needed before a definite rule could be made.

The chemical or physico-chemical problem of elucidating the constitution of basic slag and determining the effective components is more difficult.

It has always been assumed that the phosphate was the effective constituent, this being the only one of the three common fertilising constituents—nitrogen, phosphorus, and potassium—present. Some importance used to be attached to the free lime until it was realised that not more than 2 to 5 per cent. of free lime is present, so that the amount added to the ground is negligible. The Bessemer slag, however, produced effects on heavy grassland which could not be obtained by equivalent dressings of mineral phosphate or superphosphate. It is necessary to find some explanation for this result, and usually in Great Britain it is assumed that the phosphorus in basic slag is in the form of a silico-phosphate which may be assumed to differ in physiological action from the ordinary phosphate. Hall and Morison* have shown that silica affects the intake of phosphorus by the plant; and the increased assimiliation they obtained when silica was added to phosphate may offer an explanation of the efficacy of basic slag on grassland.

**Proc. Roy. Soc.*, 1909, 77B, 455-477.

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In France, on the other hand, considerable attention has been devoted to other constituents besides nitrogen, phosphorus, and potassium. Mazé maintains that a large number of elements, in addition to those ordinarily recognised, including boron, aluminium, fluorine, iodine, chlorine, silicon, manganese, and zinc, are necessary for the full growth of the plant. Other workers have experimented with some of these as fertilisers, and have shown that manganese† and fluorine‡ compounds may give increases in crop. From the published details in the French papers it is not evident that such increases would usually be obtained in the field, but in so far as they are obtainable at all in soil, they indicate that other constituents of slag besides phosphorus are effective. Indeed, the manganese content of slags is actually determined in France.

The experiments made in England with manganese compounds as fertilisers have not led to promising results. At Rothamsted manganese dioxide and manganese sulphate were both tried: both succeeded to a small extent in pots, but failed in the field. At Woburn, also, some degree of success was obtained in the pot experiments. We do not, however, know of a single case in this country where manganese salts have given unexceptionable increases in crop in the field. It may always happen, however, that other compounds would be more effective, and we have started in the pot culture house a series of experiments with slags of known manganese content in order to ascertain whether manganese in the form in which it occurs in slag behaves in any way differently from the oxide or sulphate.

The idea has been put forward (probably by some of the slag grinders) that the composition of basic slag is less important than the state of grinding. It is true, of course, that a certain degree of fineness is necessary in order that the slag may have some chance of acting: Collins§ has adduced some evidence that the standard sieve of 100 meshes to the inch affords the best results: more extended experiments, however, might well be made. But there is no evidence whatsoever for supposing that fineness of grinding is the sole factor or is anything more than an important secondary consideration. It has been asserted that a 20 per cent. slag finely ground would have exactly the same effect as an equal weight of 30 per cent. slag finely ground, and therefore that the low-grade slag ought to find just as ready a market as the higher grade slag. Hitherto the claim has not been taken sufficiently seriously to justify any special investigation, and the direct experiments have always been with quantities of slag containing the same amount of phosphorus.

There is, however, no indirect evidence even remotely suggesting that the addition of 5 to 10 cwt. per acre of a mere gritty substance would have any appreciable effect on the soil. Many attempts have been made in the past to improve clay soils by the addition of sand: they broke down because the amounts needed per acre were not a few cwts., but many tons. The alteration of soil texture by addition

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Annales Inst. Pasteur, 1919, *33*, 139-173.

†For manganese, *see* W. E. Brenchley, Ann. Bot., 1910, *24*, 571-583; F. P. Dearrick, Cornell Univ. Ag. Mem., 1919, *19*, 371-402; J. S. McHague, *Journ. Ind. Eng. Chem.*, 1919, *11*, 332-5.

‡For fluorine, *see* A. Gautier and P. Clausmann, *Compt. Rend.* 1919, *168*, 976.

§*Plant Products and Chemical Fertilisers.* London, 1918.

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of inert particles is very difficult, necessitating large amount of material.

Reviewing all the evidence, I see no reason to depart from the customary British method of regarding the phosphorus as the essential fertilising constituent in basic slag, though I am prepared to admit that a silico-phosphate might have a special fertiliser value, and that the basic nature of the slag is also important; as to the manganese, I have an open mind, and we are starting a series of experiments at Rothamsted on this problem.

Assuming phosphorus to be the essential fertiliser constituent, it is by no means easy to discover the form in which the phosphate exists in the different slags, or even to solve the purely analytical problem of devising a method which shall discriminate between one slag and another. In the early days there were attempts in Germany to mix cheap mineral phosphate with basic slag and to sell the mixture as a genuine article. The late Professor Wagner then devised his well-known citric acid test for basic slag, which has become the standard method in most countries ever since. But, as Mr. Scott Robertson has shown, it does not help much for the evaluation of the new kinds of slag, and a new method seems called for.

Perhaps the most pressing problem, however, is the enrichment of basic slags poor in phosphate. In the case of the Bessemer slag this problem does not arise, because it is to the steel maker's interest to have a pig iron rich in phosphorus, and hence the slag is necessarily rich. But in the basic open hearth richness in phosphorus is not essential; indeed, it is not even desirable, and the steel maker takes no steps to ensure a phosphatic pig iron. When it is suggested that the phosphorus content of the pig iron might be increased deliberately with a view to improving the slag, the steel maker points to the relative prices of steel and slag, and reminds one that the tail must not be allowed to wag the dog. Agriculturists must remember that basic slag is a very subsidiary part of the steel maker's business, and that it cannot for a moment be allowed to increase the time necessary for making the steel, nor in any other way to increase greatly the cost of working.

On the other hand, the steel maker should realise that the agricultural demand for good basic slag is likely to be greater than the supply. The consumption of basic slag has greatly increased during the war, and there is no sign yet that the limit has been reached. The figures for the consumption in the United Kingdom are, in tons per annum:—

Pre-War	Year ending May 31st, 1918	1919	Estimated amount utilisable: Sir T. H. Middleton	Sir Chas. Fielding
263,000	500,000	540,000	892,000	1,463,000

It would be interesting to know from the steel makers what amount of slag calculated in terms of a slag containing 20 per cent. P_2O_5 is likely to be producible in the near future. There are two distinct cases where enrichment would be desirable:—

(1) Slags containing less than 8 per cent. P_2O_5 which at present are hardly used; by enrichment these might become worth grinding.

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(2) Slags containing 8 to 12 per cent. P_2O_5 (*i.e.*, 17.4-26 per cent. tricalcic phosphate), which are already easily saleable, but which when sold on the basis of P_2O_5 content cost a disproportionately large amount in bagging, grinding, and freight.

Assuming enrichment of the pig iron to be out of the question, the only two possibilities seem to be:—

(1) Fractionation of the slag so as to concentrate the phosphorus as much as possible in one part of the slag.

This gives a product which can be more profitably handled by all concerned, though it does not increase, but rather diminishes, the total phosphorus supply.

(2) Enrichment of the slag by adding finely ground mineral phosphate in the ladle.

We are not yet in a position to pronounce a final opinion on this latter method. In its favour may be urged the fact that mineral phosphates have distinct fertiliser value, which is apparently increased by ignition, and might well be increased by any interaction taking place in the ladle.

Against it is the difficulty of detecting fraudulent additions of mineral phosphates to slag, which might become common if there were any great difference in unit price between slag phosphate and mineral phosphate—and without some difference there would be little inducement to the steel maker to enrich his slag.

A further and perhaps more difficult problem is to improve the fluorspar slags, which at present are much less soluble in citric acid than those made without additions of fluorspar. Although these insoluble slags have a higher fertiliser value than was anticipated from the old citric acid test, they do not appear to be as effective as the more soluble ones. Not only is there a falling off in yield, but probably also in quality of the crop. Pot experiments indicate that the plant takes up less phosphoric acid from an insoluble fluorspar than from a more soluble one; agricultural experience shows that increased assimilation of phosphoric acid increases the value of the crop as animal and probably as human food.

Should it be impracticable to improve the fluorspar slags, there is still another possible solution. Agriculturists could no doubt find the precise soil and climatic conditions under which they would prove most effective, and efforts could then be made to confine their use to those particular cases.

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DISCUSSION.

The Chairman: I think it will be desirable to take the main discussion at the end, but before we go on, I will call on some of the steel authorities present to reply to some of the queries raised by Dr. Russell.

Dr. J. E. Stead: I must confess that I have listened to Dr. Russell's statement with very great interest. With regard to his suggestion of improving insoluble slags containing fluorspar, I am sure I shall be supported by all steel makers when I say that we do not see how it can be done. With regard to increasing the phosphoric acid in the slag, very early on in the history of the Bessemer process I actually patented a method of adding rock phosphate and silica to the Bessemer slag to increase the solubility and amount of phosphoric acid, the object being mainly to utilise the very insoluble rock phosphate, but steel makers would not have it. Dr. Russell is quite right in saying that "the tail must not wag the dog," and that was the answer given when I suggested we should use this method. Therefore nothing was done in that direction. For the purpose of this discussion I wrote to the Leeds Steel Co., who are producing a rather soluble, rather rich slag by a duplex process. They are doing what Dr. Russell suggests; they are fractionating the slag, in a sense, into two parts. They first of all take the liquid iron and blow it in an acid lined converter and reduce the silicon from about 2 per cent. to 0.3 per cent. They get a very siliceous slag. Then they pour off the metal into a ladle and dispose of the useless siliceous slag and put the metal into a basic lined converter and blow it in the usual way. The trouble then arose, that, having taken out the silica, the slag was not nearly so soluble as if it were left in. They made a slag which was rather rich in phosphoric acid, and the question arose as to how it could be made soluble. They tried to incorporate silica in the fluid cinder, but, do what they would, they could not get the sand to combine with the slag. They have no means of heating the slag after it leaves the converter, and therefore it was just luck whether the sand was properly mixed or not. The result depended on the human factor. You know very well what the workman is. If he is told to add so much sand per ton of slag, he will put it in as rapidly as possible rather than distribute it with care, and the consequence is that you will have a pocket of sand which is only useless matter, and very little silica combined with the slag itself. The increase of solubility by this method by adding 10 per cent. sand was only about 7 per cent. of the total of the phosphoric acid. They say that for many years they have not used that method, and they do not propose to use it again. They cannot get the silica to combine. The question raised by Dr. Russell with regard to putting in phosphate is also discussed in Mr. Robertson's paper. It is suggested

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that the phosphate should be incorporated in the molten slag, but you would have the same trouble there again as the Leeds Steel Co. had on using sand, and I am perfectly certain there is no method of incorporating phosphate with the liquid slag so as to make a homogeneous mixture. The only way that I can see is the second method suggested by Mr. Robertson, and that is to mix the mineral phosphate and the slag together when cold and grind them together. There would be no difficulty in charging them into the hopper in the exact proportions required. The suggestion is that they should be ground separately and mixed together afterwards, but that would be increasing the labour, and I doubt very much whether you would get so good a mixture Grinding them together is the best possible way to get them incorporated. The one question which arises is how much phosphoric acid or mineral phosphates must be put in in order to satisfy the farmer. We know that all experiments have shown that phosphates are soluble, and if they are soluble we may assume that the plants will utilise them in the soil. In fact, experiments show that they are utilised in that way, but so far as making the mineral phosphates more soluble by putting them inside molten slag, I think that must be dismissed.

Mr. D. Sillars: I have listened to Dr. Russell with very great interest, and he has answered a number of questions which I was rather anxious to hear answered. He has himself, in turn, asked a number of questions, some of which we shall not be able to answer. Others I may at least be able to throw some light on. As regards the quantity of slag per annum, I think that is a question which should be left. It is not difficult to answer, but it requires a little consideration as to what you would consider a minimum percentage of fertiliser in the slag. Very often the question of the trouble you are going to take to recover the slag is involved. You may recover 70 per cent. of the slag made, fit for grinding, or 80 per cent. under good conditions. Under inferior conditions of equipment in the works you may get only 40 or 50 per cent. of the slag recovered. Consequently it becomes a question of what the steel maker provides in the way of plant, ladles, locomotives, slag tips, etc., and possibly cleaning apparatus in order to make this slag fit for use. The question of whether low grade slag can be enriched was raised by Dr. Russell. I myself, as a steel maker, would be no party to putting mineral phosphate into a steel furnace. In a communication I hope to make later, I shall point out the reasons for that, but they are not any more than has been said by Dr. Russell, who appreciates the reasons for it. He also refers to fractionating, which is carried out in some steel works, and he suggests that the loss of the second and inferior slag ought not to be allowed, but that it should be enriched. It is possible that low grade slag might be enriched to, say, 10 per cent. Dr. Stead has pointed out what is perfectly true, that the excess of lime makes the slag more insoluble, and that the addition of a siliceous body to take up the excess lime renders the slag more soluble. An attempt has been made to solve the difficulty of intimate mixing by blowing finely divided silica (dry brown sand) in a fine stream on to the stream of molten slag as it comes from the ladle, the apparatus operates like a sand blast. This is the most effective method of mixing I have heard of, and it would seem

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quite possible to project a mixture of ground mineral phosphate with sufficient silica to render the phosphoric acid soluble into the stream of molten slag.

A method of increasing solubility by agitating the slag with sand is described in a December, 1919, issue of *Stahl und Eisen;* it is practised at Peine Works in Germany. The mixing is done by a mechanical stirrer, and figures are given to demonstrate that simple additions of sand without agitation do not increase the solubility of the slag.

Dr. Stead: Was that basic Bessemer or open hearth?

Mr. Sillars: Basic Bessemer.

Dr. Stead: That is very much easier.

Mr. Sillars: It is only easier so far as the surrounding equipment is very much more easy to handle.

With regard to fluorspar slags being made soluble, I think the villain of the piece is sitting here. I believe it was Mr. Saniter who introduced fluorspar into steel to remove the sulphur, and that gives us a clue as to how to do away with fluorspar.

Mr. Saniter: By doing away with Mr. Saniter.

Mr. Sillars: The difficulty starts with so many of our fuels being very high in sulphur, and if we begin at that end by cleaning the coal we get back to the question of fuel economy. If we can reduce the sulphur in coal and enrich the native ores with ore from abroad, then we can reduce the sulphur content and do away with the idea of removing the sulphur in the basic open hearth process at all. Then I think we should find fluorspar no longer absolutely necessary.

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The following paper by **Professor Cecil H. Desch, Ph.D., D.Sc.,** was communicated by the Chairman:

THE PHYSICAL CHEMISTRY OF BASIC SLAGS.

By Cecil H. Desch, D.Sc.,

Professor of Metallurgy in the University of Sheffield.

Any account of the physical chemistry of basic slags at the present day must of necessity be largely a confession of ignorance. We are still unaware, in spite of much excellent research work on the subject, of the form in which the principal components are combined in the slag. The chemical analyses indicate the proportions in which the metallic and non-metallic oxides occur, and the sulphur percentage is also known, but there is much difference of opinion as to the nature of the silicates and phosphates which compose the slag, and as to the nature of the sulphides which occur in it as minor constituents. Large and very perfectly formed crystals have been isolated in certain instances, but it is not clear that these are identical with the usual constituents of massive slags, or even that they are mineralogically homogeneous substances. As an illustration of this last point, the case of the large and apparently perfectly formed plates sometimes found in tap cinder from the puddling process may be mentioned. Microscopical examination of these plates in transverse section proves them to be intergrowths of fayalite and ferrous oxide or magnetite, resembling the "colonies" of eutectic in white iron, which also have the appearance of definite crystals, but have been shown by Professor Benedicks to consist of two constituents, closely intergrown.

The essential components of basic slag are the oxides of iron, manganese, calcium, magnesium, silicon, and phosphorus, whilst sulphides of calcium and manganese, and calcium fluoride, may be regarded as accessory components. Only one state of oxidation need usually be considered, but iron may present itself either in the ferric or ferrous form.

As a starting point, the excellent investigation of acid open hearth slag by Messrs. Whiteley and Hallimond* may be taken. It is shown by these authors that iron occurs chiefly in the form of the orthosilicate, Fe_2SiO_4, fayalite, with which the corresponding manganese compound, Mn_2SiO_4, tephroite, forms solid solutions. When the proportion of manganese is high, the metasilicate, $MnSiO_3$, rhodonite, is formed, and this may contain some iron in solid solution, but a distinct ferrous metasilicate is not observed. This is confirmed by the present writer's observations of puddling cinders, in

*J. H. Whiteley and A. F. Hallimond, *J. Iron & Steel Inst.*, 1919, i, 199.

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which a metasilicate has not been found, even when large proportions of silica are deliberately added. Any such excess appears, both in cinders and in slags, as free silica, usually in the form of tridymite. Excess of iron oxide appears as magnetite, or as solid solutions of similar character, ranging from nearly pure ferrous oxide to crystals richer in ferric iron than magnetite. The growth of such crystals is very characteristic, and they form delicate branched crystallites. In acid slags containing more than 8 per cent. of lime, an anorthic metasilicate of calcium, magnesium, iron and manganese is formed, giving to the slag a marked acicular structure. A later paper by the same authors* shows that eutectics are formed between fayalite and magnetite, and between fayalite and tridymite. The writer has also observed these eutectics, but the further eutectics mentioned by Whiteley and Hallimond, namely, of magnetite and tridymite, and of all three minerals, may perhaps be attributed to imperfect equilibrium. Should they prove to occur in the system in a state of equilibrium, then ferric oxide must be regarded as a separate component.

Leaving aside the question of phosphorus, the basic slags differ from acid slags chiefly in containing a much higher proportion of lime. A glance at the ternary equilibrium diagram for the system lime-magnesia-silica† will show that a slag containing anything like 40 per cent. of lime must be largely made up of the orthosilicate, Ca_2SiO_4. The solid solutions of this silicate with the silicates of other metals are very liable to undercooling, with the formation of glass. Consequently, a glassy ground mass is often observed in basic slags, rendering the interpretation of their constitution much more difficult. Acid slags are usually very free from glass, and even puddling cinders mostly contain mere traces of it. Sections of basic slag may exhibit glass in which are embedded small crystals of a phosphoric mineral; and it is evident that the constitution of such specimens could only be determined by making experiments in the direction of annealing, and so permitting the crystallisation of minerals from the glass.

Turning now to the phosphorus, it is remarkable that no phosphate of iron, either ferric or ferrous, is known which is stable at high temperatures. The naturally occurring phosphates are hydrated minerals, and do not yield homogeneous anhydrous products on heating. On the other hand, the phosphates of calcium are well known. Several investigators, however, have shown that silicophosphates are the principal constituents of phosphoric basic slags. The first of these compounds was described by Carnot,‡ who attributed to it the formula $Ca_3(PO_4)_2$, Ca_2SiO_4. In 1887, Stead and Ridsdale§ described crystals of a compound also containing phosphate and silicate, $4Ca_3(PO_4)_2$, Ca_2SiO_4. Other similar compounds have been described, and their composition is reviewed by Kroll,‖ who added yet another, Thomasite, to which he attributed the composition

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* J. H. Whiteley and A. F. Hallimond, *J. Iron & Steel Inst.*, 1919, ii., 159.
† J. B. Ferguson and H. E. Merwin, *Amer. J. Sci.*, 1919 (iv), *48*. 81.
‡ A. Carnot, Richard and Daubre. *Compt. Rend.*, 1883, *97*., 136.
§ J. E. Stead and C. H. Ridsdale. *Trans. Chem. Soc.*, 1887, *51*.. 601.
‖ V. A. Kroll, *J. Iron & SteelInst.*, 1911, ii, 126.

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$Ca_3(PO_4)_2$, $3CaO$, Ca_2SiO_4. At an earlier period, Hilgenstock* had described a tetrabasic phosphate, $4CaO$, P_2O_5, and this was long regarded as the essential constituent of all slags which were of agricultural value. It is more likely that the silicophosphates are the valuable compounds. As a rule, these compounds have been described by their external characters only, and very little is known as to their mineralogical individuality. It must be remembered that calcium is replaceable to a greater or less extent in such compounds by iron and other metals, and it is quite possible to find slags, the analysis of which will permit of inclusion under the formula of Thomasite given above. It does not follow that these slags are pure individuals; they may be eutectic intergrowths simulating pure crystals, as mentioned above. When phosphorus is added in moderate quantities to puddling cinders, no new constituent makes its appearance, and phosphorus compounds can evidently pass into solid solution in siliceous iron minerals. The examination of specimens polished on one surface only and etched, as in the examination of metallographic specimens, usually gives much more information than the study of thin sections, although the application of polarised light to the latter affords a useful means of identifying minerals by their optical properties when their limits have been once defined. The fine eutectics in slags and cinders are generally overlooked in thin sections.

Sulphides enter into solid solutions to an unknown extent, but a part may remain in insoluble globules. Fluorides combine with phosphates to form minerals of the apatite class, and this no doubt accounts for the insolubility, under agricultural conditions, of slags containing fluorspar. Beyond this, little can be stated definitely as to the constitution of the basic slags without further research, the performance of which is highly desirable.

*G. Hilgenstock, *Stahl u. Eisen*, 1883.

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Sir Thomas H. Middleton, K.B.E., read a paper on "The National Aspects of the Case for Increasing the Supplies of Basic Slag."

THE NATIONAL ASPECTS OF THE CASE FOR INCREASING THE SUPPLIES OF BASIC SLAG.

By Sir T. H. Middleton, K.B.E.

Several of the papers contributed to to-day's discussion deal with the uses and effects of basic slag as a fertiliser. I propose to approach the subject from a somewhat different standpoint, namely that of the increase of tillage land and of our supply of home-grown food. The supply of basic slag is one of three controlling factors—the others being the prices of cereals and wages—in the agricultural situation of to-day.

I propose in the first place to place before you a few figures bearing on the question of our present supplies of home-grown food, next to allude to the influence of basic slag in improving pastures, and then to show the connection between these subjects and the future course of tillage farming.

Food produced by Soils of the United Kingdom.

From figures published in the annual volumes of statistics issued by the Board of Agriculture and Fisheries, and in the Report of the War (Food) Committee of the Royal Society, it may be shown that in the period before the War (1909-13) the soils of the United Kingdom were supplying products which measured in terms of energy would have sufficed for the support of about 17½ million persons. The whole population to be fed averaged about 45¼ million persons; thus in each week the home supply would have sufficed from Friday night until Monday morning. As I have elsewhere said, we had become a nation of self-suppliers for the week-end!

It is interesting to compare the position before the outbreak of war with the condition of the food supply during the last great war in which the country was engaged. An examination of our imports in the early part of the nineteenth century shows that in 1801-10 the soils of the United Kingdom must have fed on an average some 16½ million persons. After Waterloo there was a rapid increase in our industrial population, and an enormous pressure on the means of subsistence. During the past 25 years writers on political and social subjects have had much to say of the iniquities of the period which led up to the "hungry forties." I shall not attempt to defend the action of the "greater villain" "who stole the common from the goose," but when we criticise agriculturists who are reported to have robbed the people, let us at least be fair, and let us admit that their energy enabled them in the period 1830-40 to feed a huge population. The "hunger" of the "forties" was not due to the incapacity of our farmers. The fare on which indus-

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trial England grew into a prosperous nation may have been meagre; it was ill-distributed, no doubt, and there was much hardship; but, viewed from the standpoint of to-day, the feat performed by our farmers in the period of reconstruction that followed Waterloo was astonishing, for by 1835 they maintained 24½ millions on the soils of the United Kingdom; in other words, nearly 50 per cent. more than at the outbreak of the Great War.

Taking the soils of the United Kingdom as a whole, it may be shown that before the war, they were providing for from 35 to 40 persons per 100 acres. In an estimate made in 1916 I found that, whereas 100 acres under the plough, *i.e.*, under other crops than grasses and clovers, maintained about 84 persons, a similar area under grass provided for from 17 to 20. I have not revised this particular estimate with the fuller figures now available; but an estimate recently made by another method leads me to think that my 1916 comparison was somewhat too favourable to grass, and that in the period 1909-13 rather fewer than 17 persons were actually supported by the average 100 acres of our cultivated grass land.

I do not propose at present to argue out the national aspects of grass and tillage farming. Speaking from a farmer's standpoint, I am prepared to agree that in many parts of the United Kingdom the advantages of grass farming are obvious, for it must be remembered that the food problem as the farmer sees it is not the feeding of our 46,000,000 people, for they have long ceased to be dependent on his efforts, but the feeding of his cattle, sheep, and other live stock. The two main human foods grown by the farmer —wheat and potatoes—occupied no more than 3,000,000 acres in the period before the war, while 36,000,000 acres were devoted to the crops required by his cattle and sheep. The value of the two tillage crops was about £27,000,000, while his live stock brought him in some £125,000,000.

Under these circumstances, the importance to the farmer of grass, the natural food of his live stock, needs no demonstration. Since grass is so important, its present quality and the scope for improvement are points to which I wish to direct your attention to-day. The methods of improvement will be discussed by others. I shall content myself with referring to certain general aspects of the subject.

The Scope for Improvement in our Pastures.

So far as I am aware, there are no trustworthy records from which the average production of meat by our finest permanent pastures can be estimated.

The best fattening pastures that I personally have met with are in the Market Harboro' district of Leicestershire, and I estimate that the richest field in this district, which I examined, would on an average of years produce from 180 to 200 lbs. of meat without the assistance of oilcakes. The field in question fattened a bullock per acre in the early part of the grazing season, made a "forward store" without oilcake, or a fat beast with oilcake in the autumn, and in addition would provide some keep for store cattle or sheep in the winter months.

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How many of our 33½ million acres of grass land come up to the level of the pasture described above? If one were to form an estimate from the newspaper controversies that centred round the ploughing up of grass land during the course of the war, one would probably be prepared to believe that about one-third, or possibly even one-half, of the grass land of England was of fine quality. In spite of the careful way in which the Agricultural Executive Committee in most cases selected land for ploughing, one heard constantly of their errors in destroying fine grazings to provide land for corn. Their task was to select no more than 1/8th of the grass land of England and Wales for ploughing, and although, notwithstanding their efforts, less than two million extra acres were in fact ploughed up, it was freely alleged that the live stock interests of the country were being jeopardised to provide wheat and oats. Clearly, if one believed all this war-time evidence, the pastures of England were a national heritage of great value. But let us test the position in another way. Is it possible that anything like one-third of our pastures can be up to the level of the " one-fat-bullock-per-acre " standard? What are the results of the grazing industry? The total number of grass-fattened cattle marketed in the United Kingdom does not exceed one million per annum, and it is common knowledge that a large percentage of this number is fattened with the help of oilcakes. Personally, therefore, I should be surprised to find that there are in fact 500,000 acres of grass land in this country which, without the help of concentrated feeding stuffs, fatten one bullock per acre on the average of a series of years.

Now, what about the other end of the scale? What yield may be expected from our poorest cultivated pastures—I do not refer to our 15 million acres of hill grazings, which probably produce less than 5 lbs. lean meat per acre per annum, but to our so-called cultivated land. I followed Dr. Somerville and preceded Professor Gilchrist in the management of some poor pastures in Northumberland. Professor Gilchrist will no doubt deal with its productivity in the paper which he will give us; but I may say that my own estimate is that land of this type—poor clay soil pasturage very common in the North of England—yields from 15 to 20 lbs. of lean meat per acre in the course of a year. Other experimental pastures in Northamptonshire and Cambridgeshire which I have had an opportunity of studying produced from 20 to 25 lbs. of lean meat in an average season, and from the opportunities I have had of inspecting poor pastures in other parts of the country, I have come to the conclusion that there are very many thousands of acres of grass land in the United Kingdom from which the nation obtains no more than 25 lbs. lean meat in the course of a season.

With the information at present available, it is not possible to make any close estimate of the average production of meat on the pastures of the United Kingdom. In the first place we do not know the total production. In the five years before the war it was estimated at 1,150,000 tons of beef and mutton, but with the more accurate information at the disposal of the Ministry of Food, it was found that in 1919 we produced some 875,000 tons only. There has been a considerable reduction in the number of sheep, especially

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of the larger sheep fed in the South of England, but the number of cattle is practically the same as in 1914. Feeding stuffs were scarce, and cattle were smaller than before the war. But when full allowance has been made for these circumstances, it is not possible to resist the conclusion that we over-estimated our meat production in the period before the war.

Even if we knew the total output of meat, it would be necessary before estimating the production of our grass land to ascertain (1) the production on hill grazings, (2) the yield from the products of arable land, and (3) the amount due to imported feeding stuffs. Though it is possible to make more or less satisfactory guesses at the yield from each of these sources, it will be evident that no great accuracy can be claimed for the final result of an estimate that has in view so many uncertain factors. On the basis of the estimated pre-war production of meat, my former view was that our pastures produce on the average 100 to 110 lbs. of lean meat per acre per annum, but at present I am disposed to think that 90 to 100 lbs. would be nearer the mark.

Moreover, the meat of the " average " pasture is very different in quality from that produced on the finest pasture. The food value of the lean meat from our " average " grazings is probably not more than two-thirds that of the fat meat of feeding pastures. Hence my opinion is that our best pastures have about three times the value of our " average " pastures as sources of human food, while they are 10 or 12 times more productive than the poor pastures that replace the former corn lands of many parts of the country. In any case, anyone who has investigated the subject will be prepared to admit that our pastures offer great scope for improvement. Let me illustrate this point. In 1902 I laid out four ten-acre fields on the unimproved pastures at Cockle Park, Northumberland; basic slag and other manures were applied. This land in its unimproved state produces about 20 lbs. lean meat per acre per annum. Records have been kept ever since, and Professor Gilchrist will no doubt allude to some of the lessons to be learned from a study of these records; but I propose to refer to one point only. It is that on the average of two of the plots, and during the 11 years 1904-14, the live increase made by cattle and sheep on these 20 acres was equal to about 105 lbs. of meat per acre, or more than five times the yield of the untreated land. The special interest of this experiment for us to-day is that the improvement was due to basic slag. The results of many other experiments might be cited to prove that on thousands of acres of this country the yield might be equally increased by the proper use of basic slag.

The effect of the application of slag to some types of pastures is so striking that the results have been described as magical; but there is no " magic " in its action. It depends on the habit and manner of growth of white-clover on land that has been depleted of phosphates by corn growing, and has then been left to " tumble down " to grass.

I am not, however, at present concerned with the mode of action of basis slag, but with the results; and most agriculturists will agree that, in conjunction with white clover, it is the most potent agent known for restoring fertility to worn out corn land. If the

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old corn growing lands of England are again to take their place in producing wheat, it seems probable that one feature in the scheme of management to be adopted will be the alternation of corn growing with a period during which clay soils will rest and regain fertility by growing clover manured with basic slag.

Effect of Pasture Improvement on Tillage Farming.

Apart from the uncertainty as to the future cost of labour, the chief obstacle to the expansion of tillage in this country is the difficulty that farmers would experience in devising means for supplying their live stock, were they to be deprived of any considerable proportion of the existing grass land. It is well known that, given the necessary skill and the command of capital and labour, food for live stock may be raised in greater quantity from land under the plough than from grass; but it is certain that in many instances stock could not be kept so cheaply as they now are were grass land to be broken up, and it is further certain that the life of the stock farmer would be less easy if tillage crops replaced his pastures. Any policy which aims at extending the cornfields of England must therefore reckon with strong opposition, if the increase of corn means the decrease of grass and hay. But it seems to me that the area under corn could be largely extended without reducing the natural foods of our live stock; for, given enough basic slag, it would be an easy matter to restore all the land well adapted for corn growing to tillage, and to grow as much grass and hay as we do at present. Let us examine this statement.

In the early seventies of last century England and Wales had about 15 million acres under the plough. Before the war the area had fallen to 11¼ million acres. In 1918 it had increased to 12½ million. Although labour is less plentiful and much more expensive than in the "seventies," there should be no difficulty, given remunerative prices, in again reaching the 15 million level. For in the interval the farmer's command of machinery and of manures have both greatly increased. In the immediate future the lack of buildings would prevent any considerable extension of tillage, but a time will come again, it may be anticipated, when builders will be glad to secure work, and when materials will be forthcoming. It is, I think, beyond dispute that 15 million acres of land suited for tillage could be found; what the farmer argues is that in view of the increase in his herds he could not carry on his business with 12 million acres of grass in England and Wales; he wants to have the 16 million he had available in 1914. As I have already indicated, I admit the difficulty. I do not say to him: "The extra 4 million acres under tillage would feed as many animals as the 4 million acres grass ploughed up." In theory it could do so; in practice the farmer might not succeed in the attempt. What I should prefer to say is: "Given manure and reasonable management, there will be no difficulty in growing as much grass and hay on 12 million acres in future as you produced on 16 millions before the war."

Is this statement of the case reasonably probable? Let me give the grounds for my belief that it is.

Of the 16 million acres under grass at the outbreak of war there may have been one million so good that no marked response

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to manuring could be expected, and 3 millions on soils so dry and arid that no scheme of manuring would prove profitable. This would leave a balance of 12 million acres susceptible of profitable improvement. In view of the wide extent of our clay soils and chalk pastures, and the extraordinary response which most pastures and meadows of this type make to the application of basic slag, it seems to me to be reasonable to assume that if 4 million acres were ploughed, the remaining 8 million acres could grow as much grass as is now being produced on the whole 12 million acres

Value of Extra Tillage Land to the Nation.

The value to the community of these 4 million extra acres under the plough would be much greater than at first might be supposed. The full effect is not apparent from the simple proportion 11 : 15.

Opponents of a plough policy usually start off with the assumption that the corn-growing capacity of Britain in proportion to her needs is so small that any effort which might be made to increase home supplies would be negligible. This assumption is far from being correct.

I estimate that if the necessity arose, and all the products of the soil were carefully rationed and efficiently distributed, the present population of the United Kingdom could be supplied with breadstuffs from the produce of about 14 million acres. Towards this total England and Wales would be required to contribute 10 million acres. Now, with 11 million acres under the plough, as in the pre-war period, and with the system of farming then current, we would normally grow 5¾ million acres of grain. Should high prices continue to rule, it is probable that 6¼ million acres would be forthcoming. With 15 million acres under the plough, we would grow from 7½ million acres when corn prices were low to 8½ millions, or even 9 millions, when prices ruled high (the average for the period 1871-75 was 8,100,000 acres). Should danger arise it would be impossible to secure 10 million acres of corn if we started, as in 1914, with 11 million acres of tillage land. In spite of the great effort made, we only got 7½ million acres in 1918. But if we began with 15 million acres of tillage in hand, our task, though formidable, would be by no means impossible. An extensive grass-ploughing campaign would be called for, but we should start on our effort to secure two or three million extra acres of corn, with the buildings, the men, the horses, and the machinery which 15 million acres of tillage would support in time of peace, instead of with the men and equipment of 11 million acres.

In a war crisis, therefore, these extra four million acres of tillage land would mean the difference between the provision of a sufficient, if meagre, supply of breadstuffs for the whole population, and a curtailment of the supplies that would lead in the first place to a breakdown of the machinery for rationing and later to famine and to the popular ferment that would inevitably seize a people deprived of a sufficiency of bread. It would mean the difference that there was between our own comfortable, if somewhat unattractive, diet in the last two years of the war, and the makeshifts on which our enemies attempted to fill, but failed to feed, themselves.

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But, it will be argued, "why prepare for another great war when we have made an end of great wars, and why suppose that if there is a war, imports will not reach us with as great certainty as they did between 1914 and 1918? We have shown how to defeat the submarine, and we can safely rely on our Navy and merchant vessels in any circumstances that can arise." Let us admit this argument, and examine the case for the extra 4 million acres as a peace proposition.

On the lavish scale on which this rich nation fed itself and its livestock in the period 1909-13 I estimate that some 21 million acres growing "average" (*i.e.*, average British) crops would be wanted to supply the cereals consumed in the United Kingdom. The area under these crops in the United Kingdom in 1909-13 was between 7½ and 8 million acres. About 2 million acres were contributed by Scotland and Ireland. As I am discussing the subject from the standpoint of England and Wales only, we may assume that their share in the 21 million acres that would be called for if all our cereals were home grown, would be between 17 and 18 million acres. The actual contribution made by England and Wales in the period 1909-13 was 5,800,000 acres. Under the influence of high prices this area might be increased to 6¼ million acres, *i.e.*, to 36 per cent. of the area required for a full supply.

Having regard to the large proportion of our area under permanent grass, and the demands which livestock fed on poor grass land make on the products of arable land, it is unlikely that even if corn prices remained at the present high level and the shilling loaf were a permanency, that we would have more than 6½ million acres under grain.

Under the conditions which I have postulated for an arable area of 15 million acres, the limits of corn growing would be wider. I have assumed the improvement of some 8 million acres of pasture by 50 per cent. What I meant to convey was that 8 million acres of grass could be made capable of carrying 50 per cent. more stock during the summer season, and of producing 50 per cent. more hay. But there would be a second important result of such a change. An improved pasture has a much longer grazing season than an unimproved; the grass comes earlier and lasts later; thus, assuming the same numbers of cattle and sheep to be kept through the summer on similar areas of improved pasture that had previously been kept on 12 million acres of unimproved land, there would be a smaller demand for winter keep in the one case than in the other.

A second circumstance favouring wider variations is the area under grain crops with 15 million acres arable than with 11 millions should be pointed out. The additional 4 million acres would, for the most part, consist of the heavier soils; these are more expensive to till, and when supplies of grain were abundant and prices low, a system of rotation pastures would, and should, be adopted. I say "should," because it is just these soils that, with the assistance of basic slag and white clover, might very profitably be laid down to short leas. When supplies were scarce and prices rose, this same land would stand a good deal of intensive corn growing. Thus I estimate that while with 15 million acres of arable land the probable area under grain would vary from 7½ to 8½ million acres,

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the upper limit, if favoured by a wise national policy, might well reach 9 million acres. If, however, we adopt the more conservative figure of 8½ million acres under grain, we should still increase our home supplies by 12 to 14 per cent. An increase of this amount would not only substantially diminish our foreign purchases, but would tend to reduce fluctuations in price, for, in spite of the abuse which we bestow on our British climate, it seems to me that our own harvests may well fluctuate less in amount than the average of the exportable surplus of the harvests from which we must draw our future supplies. This is not the time to discuss the prospects of our future wheat supply, and I cannot pretend to an expert knowledge of the wheat trade, but when I look to the sources from which our supplies were drawn in the past, to the effect which war has had upon the soils and the labour that produced our wheat, and to the great fluctuations in yield due to climate, it does not seem to me that a nation which depends so largely as we have done in the past on " exportable surpluses," can escape great fluctuations in the price of bread.

Occasional high prices, even frequent high prices, will not in themselves secure the ploughing out of grass. Other measures are called for, and among the most important is an effort to increase the output of basic slag, so that the quality of our grass land may be improved.

To the steel maker the slag which he produces is no doubt a secondary consideration, but I hope that his concentration on improvements in the manufacture of steel will leave him with time and inclination to bestow attention on processes by which the quality and output of basic slag may be increased. I have endeavoured to direct attention to the national importance of basic slag, and I hope I have succeeded in indicating that its manufacture is not merely of interest to the farmer as a means of providing a profitable manure for his pastures, but that it has a direct bearing on the future of the bread supply of those engaged in the steel industry and of their fellows in our other industries. The conditions affecting the food supply of the industrial classes are very different from what they were in 1820, but they are also very different from what they were in 1914. The extent to which our urban population may be driven to rely for their supplies of food on the soils of this country cannot be foreseen. We must not too confidently assume that all that we ask for will be supplied by other countries. There may still be " hungry forties " ahead of us.

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Sir A. Daniel Hall, K.C.B., F.R.S., sent in a communication on "The Demand for Basic Slag," which, in his unavoidable absence, was taken as read.

THE DEMAND FOR BASIC SLAG.

By Sir A. Daniel Hall, K.C.B., F.R.S.

Prior to the war, the consumption of basic slag in the United Kingdom was about 282,000 tons per annum, as against a make of something over 300,000 tons. During the war the output rose to 500,000 tons per annum, the whole of which was consumed internally. At the present time this output seems hardly likely to be maintained, since in the last six months of 1919 the output showed a decline of over 40,000 tons, as compared with the corresponding period of 1918. The magnitude of the output will naturally depend upon the development of the steel trade. At the same time the period of war has been marked by a considerable decline in the quality of the basic slag produced in this country, due to the substitution of the open hearth process and the introduction of fluorspar into the melt.

The question to which I am particularly addressing myself is to form an estimate of the amount of basic slag that could profitably be employed in the agriculture of the United Kingdom, supposing that industry used the amount of manure of which a good farmer would think the land in need. Hitherto by far the largest application of basic slag has been on a comparatively poor grass land of the heavy type. As is well known, its effect in such cases is often of a most surprising character. The whole character of the herbage changes owing to the development that is induced on wild white clover, which in its turn assimilates nitrogen from the atmosphere, and so after grazing brings about a general enrichment of the soil.

The herbage changes its botanical character; not only clovers, but improved grasses begin to take the place of the rough bent grass which formerly comprised the greater part of the herbage; moreover, the feeding value of the herbage is enormously increased. The stock grow more rapidly, and stock begin to fatten on land which previously would only maintain them in rough store condition.

It is often thought that basic slag possesses no valuable effect when applied to good pastures, especially those that have already a reputation for their feeding value. Farmers report that they have tried basic slag upon such land and see no results from its application. This is due to the fact that such good pastures already contain a considerable proportion of clover plants, and the basic slag, though it may increase the amount of clover, does not effect that marked change to the eye which characterises its application to the

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poor clay pastures in which clover was previously quite inconspicuous. None the less, an effect is produced upon the feeding value of the herbage of these good pastures. Sometimes close observation will detect this, for it can be seen that stock graze more habitually upon the slagged than upon the non-slagged portions of the field. To obtain, however, a proper measure of the effect of slag upon such good pastures, it is necessary to keep a record, if not of the actual live weight increase of the grazing animals, before and after the pasture has been slagged, but at any rate of the number of grazing days the field affords, and the rate of progress of the animals. If it is a summer grazing from which sheep or cattle are sold off fat, a system of book-keeping which records the numbers of animals sold fat and the expenditure thereon, including the rent of the field, manure, the cake, and other artificial manures, should be employed. The value of a basic slag manuring upon a fattening pasture will become manifest.

Within my own experience it has been possible to replace the greater part of a heavy cake bill by a much cheaper application of basic slag, even upon some of the richest pastures in the south of England, where basic slag had no visible effect upon the character of the herbage. This result is undoubtedly due to the prominent part which phosphates play in conferring a high nutritive value upon the grass, and in this connection it may be noted that when Dr. Russell and I attempted to investigate the differences between adjoining pastures in Romney Marsh which caused one to be a feeding pasture capable of fattening a bullock and six sheep to the acre, where the adjoining field would only maintain sheep in a growing condition, one of the few constant differences to be observed was a higher proportion of phosphates in both the soil and herbage of the fattening pasture. For these reasons I am of opinion that basic slag may be profitably used on many of the good pastures of the country in a way it has not been employed in the past, and this outlet has become still more remunerative in view of the vastly enhanced cost of concentrated feeding stuffs.

Turning now to the possible amount of basic slag which could be expected to be employed in this country, we may base our calculations upon a distribution of the cultivated area of 25 million acres in grass and 21 million acres under the plough. This, of course, is not the amount of arable land that we ought to have, or to which we hope to attain, but it will serve as a basis for calculation. Of these 25 million acres, 6 million would be laid up for hay and should receive 5 cwts. of phosphatic manure every third year. Assuming that half of this is basic slag and the other half superphosphate, the annual consumption would amount to 250,000 tons. There remains 19 million acres of pasture, at least half of which would profitably respond to a dressing of 5 cwts. of basic slag once in five years. At this rate the further annual consumption of basic slag would amount to 475,000 tons.

The 21 million acres of arable land may be estimated to require $1\frac{1}{4}$ million tons of phosphatic manure annually, if the best is to be made of the land. Prior to the war it was customary to use for this purpose almost entirely superphosphate, but the experience of the last few years, when men were forced to employ basic slag to a much greater extent, has taught many farmers the value of basic

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slag upon arable land even of the lightest type. To get the best results the slag must be applied early, but the farmer who is not trusting to a single application of manure, but is building up a body of fertility in his land, can get as effective results out of basic slag as from superphosphate. Assuming, however, that only 1/5th of the phosphates applied to the arable land are to be derived from slag and the remainder from superphosphate, there would still be a consumption of 250,000 tons of basic slag upon arable land, and the total requirements are then 975,000 tons per annum of basic slag, twice as much as the production at present in sight.

It must not be supposed, however, that consumption on such a scale would be at once attained, even if the manure were available. A considerable campaign of enlightenment is even yet required before the great majority of farmers will employ fertilisers upon the scale I have indicated as likely to be profitable. The Ministry of Agriculture are already embarking upon such a propaganda, even though the amount of basic slag which they think desirable to use upon the land is not in sight.

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The following paper by **Professor D. A. Gilchrist,** entitled "Basic Slag and its Place in the Development of Agriculture," was received subsequent to the meeting:

BASIC SLAG AND ITS PLACE IN THE DEVELOPMENT OF AGRICULTURE.

By Professor D. A. Gilchrist, Armstrong College, Newcastle-on-Tyne.

The following are extracts from a paper on "Basic Slag as Affecting Agricultural Development," read to the Society of Chemical Industry on February 5th, 1917, by Professor Louis and myself:—

"Phosphatic manures have enormously developed the production of farm and garden crops. Soils can obtain nitrogen by the growth of leguminous plants, and to a certain extent, by other means without the direct addition of nitrogen to the soil; but the phosphates removed by crops must be returned by direct manuring, and farmyard manure does not return these phosphates in a sufficient manner, because so much of these are retained by the animal. Bones and bone ash were used to some extent to replace phosphates early in the nineteenth century. When Liebig and Lawes, about 1840, found that bones and mineral phosphates could be rendered more effective by treatment with sulphuric acid, so as to make part of the phosphates soluble, an enormous impetus was given to the growth of swedes and turnips, the crops of which were greatly increased by the judicious application of soluble phosphates (superphosphate) upon soils where phosphate exhaustion had been long in progress. Worn-out pastures, also suffering from phosphate exhaustion, gave a remarkable response to these phosphatic manures. When superphosphate had been used for a considerable time, it came to be realised that this manure did not give as good results on peaty soils or on soils poor in lime as on soils in which a fair amount of lime was present. The conclusion was therefore reached that the soluble phosphates in superphosphate gave the best results when they were precipitated into insoluble phosphate in the soil, and were thus well distributed in the soil in a fine state of division."

"Until about 1880 the supply of phosphatic manures was met to some extent by bone meal, but chiefly by mineral phosphates, the bulk of the latter being converted into superphosphate, while a small quantity was used as ground phosphates. The discovery by Messrs. Gilchrist and Thomas that it was possible to remove phosphorus from iron and to transfer it to the slag in making steel, gave rise to the so-called Gilchrist-Thomas or basic Bessemer process of steel making, and it was soon found that the slag produced in this operation possessed valuable manurial properties."

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"The late Dr. Andrew Aitken, Chemist of the Highland and Agricultural Society of Scotland, conducted trials for that Society at the Pumpherston Agricultural Station, near Edinburgh, some years before 1889, which proved that rock phosphates or mineral phosphates, when finely ground, gave quite good results. About this time, however, basic slag came into general use, and phosphate of lime could be purchased in this manure at about 9d. a unit, whereas the same in finely-ground rock phosphate cost over 1s. 2d. a unit. As Dr. Aitken found that basic slag phosphates gave better results than mineral phosphates, the use of the latter, which had begun among farmers in Scotland, was stopped, and basic slag came into general use, as it was somewhat more effective, and cost less per unit of phosphate of lime."

"At Cockle Park, on heavy loam soil of a poor character, a dressing of 10 cwt. an acre of high grade basic slag, applied once in six years, has increased the seeds hay crops by over 10 cwt. an acre in each of the three following years after its application; oats have been increased by over 10 bushels an acre in the fourth year thereafter, swedes by over 4 tons an acre in the fifth year thereafter, and barley by 4 bushels an acre in the sixth year thereafter. At pre-war prices, valuing hay at £3 a ton, oats at 3s. a bushel, swedes at 7s. 6d. a ton, and barley at 4s. a bushel, this gives a total of £8 2s. 6d. as the increased value of the crops for six years after the application of 10 cwt. high grade basic slag, which, at pre-war prices, would cost about 25s. On the sandy loam soils at the same centre, a dressing of 5 cwt. an acre of high grade basic slag has probably increased the following seeds hay crop by 10 cwt. an acre, the oats in the second year by 10 bushels an acre, the swedes in the third year 3 tons an acre, and the barley in the fourth year by 4 bushels an acre. This gives an estimated return of £4 18s. 6d. from the application of 5 cwt. basic slag, at a cost of about 12s. 6d."

"In the Hanging Leaves fields at Cockle Park, where a pasture of the poorest character has been treated with basic slag alone, the increased gains made by the cattle and sheep during the past eleven years show a gain of about 7s. 6d. for each shilling spent on basic slag."

"The foregoing estimates of increased crops from the application of basic slag are based on crop results at Cockle Park. It should be noted that the basic slag owes much of its effects to the inclusion of wild white clover in seeds mixtures. This plant is enormously developed by basic slag, and the nitrogen collected by its roots is of the greatest help to the phosphatic residues of the slag in increasing the various crops."

"The amount of basic slag now used annually for manurial purposes in this country may be between 200,000 and 300,000 tons. It has already been estimated that the total amount of basic slag produced in this country is now about 850,000 tons, but, as much of this is of low grade, the total amount produced may be equal to about 600,000 tons of high grade basic slag."

"The total area under crops and grass in the United Kingdom (not including mountain and heath land) is under 47 million acres. Assuming that 250,000 tons of basic slag are now used for agricultural purposes in the United Kingdom, this would provide a

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dressing of 5 cwt. of basic slag per acre every fourth year for four million acres. If the total basic slag produced in this country were used for agricultural purposes (estimated to be equal to 600,000 tons high grade basic slag), the total area of land so treated would be increased to 9,600,000 acres, and it can be realised from the foregoing Cockle Park figures how enormously the food production of this country would be increased."

"In this country there were produced annually before the war from 820,000 to 850,000 tons of superphosphate, of which about 76,000 tons were exported. These figures give some idea of the relative amounts of superphosphate and basic slag used before the war for manurial purposes. Superphosphate is produced mainly from rock phosphates, of which nearly 600,000 tons were imported to this country in 1913."

The following notes are extracted from two books by Dr. C. Hopkins, Professor of Agronomy, University of Illinois:—

In "The Farm that won't wear out" he emphasises that *phosphorus is the master key to permanent agriculture*. He points out that the annual export of phosphates from U.S.A. to Europe is of the value of 5,000,000 dollars (£1,000,000). He summarises trials of different phosphates at the Pennsylvanian State College (12 years), Maryland Experiment Station (12 years), the Rhode Island Experiment Station, the Massachusetts Experiment Station, and the Ohio Agricultural Experiment Station (16 years).

At Pennsylvania the yearly average gain per acre for 12 years was 2.12 dollars from raw phosphate and 48 cents from acid phosphate. At Maryland the raw phosphate produced a higher total average yield than acid phosphate at less than half the cost. At Rhode Island, hay and grain gave increases per acre of 14,580 pounds from raw phosphates and 14,550 pounds from acid phosphate on unlimed land; lime and raw phosphate produced 27,030 pounds, and lime and acid phosphate, 29,690 pounds increase; the acid phosphate cost three times as much as the raw phosphate. At Massachusetts raw phosphate ranked above acid phosphate, both as an average for the entire period, and as an average between 1895 and 1900. Where no phosphate was applied only 55 per cent. as much was produced as where raw phosphate was used. At Ohio, on the average, 320 lb. raw phosphate per acre, applied with dung on clover sod, gave the following increases:—Maize, 8.4 bushels; wheat, 4.7 bushels; hay, .49 of a ton; all above dung alone. Under the same conditions 320 lb. acid phosphate, costing twice as much money, but with only half the phosphates, gave increases of 7½ bushels maize, 6.1 bushels wheat, and .46 of a ton of hay.

On page 52 he states that the natural rock phosphate should be ground so that at least 90 per cent. passes through a sieve with 10,000 meshes to the square inch, and, of course, its content of phosphates should be guaranteed (60 to 75 per cent.). This ground phosphate he calls *Raw Phosphate*.

He goes on to state:—

"On my own farm I use about one ton per acre of raw phosphate once every six years, thus adding at least 250 pounds of phosphorus at a cost of less than 8 dollars; whereas 200 pounds of the common 'complete' fertiliser per acre yearly would cost 12 dollars every

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six years, and would supply only 40 pounds of phosphorus. I do not use 'complete' fertilisers, because there is plenty of nitrogen in the air and plenty of potassium in the soil; and because, by growing and ploughing under plenty of clover, I not only secure nitrogen from the air and liberate potassium from the soil, but also liberate the phosphorus from the raw rock phosphate applied to the soil. In beginning the use of raw phosphate where the supply of organic manures is limited, I apply one ton of phosphate and 600 pounds of kainit in intimate connection, turn them under, preferably with organic matter, then add ground limestone if needed, and thus prepare to grow clover."

The foregoing summary of this book shows that the author's main idea is that phosphates, properly applied to the soil with the judicious growth of leguminous crops, will supply all the nitrogen that is wanted, as well as the phosphorus.

Dr. Hopkins' larger work, "Soil Fertility and Permanent Agriculture," is published by Ginn and Company, New York and London. It contains excellent summary tables of all the phosphate experiments referred to in the little book. On page 595 he deals with production of phosphate rock, and states that Florida, South Carolina, and Tennessee have for several years been the main sources of phosphate in U.S.A. The production of phosphate from South Carolina from the beginning of the industry in 1867 till the year 1888, during which period that State was the only producer, was about 4½ million long tons for this whole period. In 1908 the marketed production of phosphate rock in U.S.A. was 2,400,000 long tons, and the total value about 11,400,000 dollars. About half of this was exported.

The world's production of phosphate rock in 1907 in metric tons was about:—

Algeria	374,000
Belgium (1906)	152,000
France	431,000
Tunis	1,069,000
United States	2,301,000

The foregoing information is quoted by the author from "Advance Chapter from Mineral Resources of the United States, Calendar year, 1908," by Van Horn, of the U.S.A. Geological Survey. The author further states: "It would appear certain that the phosphate deposits of the U.S. are to be drained for the benefit of the worn-out farm lands of foreign countries." The exports of deposits from Florida, Tennessee, and South Carolina cannot be easily prevented, but the author suggests that this should be done with other phosphates and even with these to the fullest extent possible.

Dr. Hopkins' works are of the greatest importance in showing the important part that mineral phosphates take in the agriculture of the United States. They point out strongly our need of conserving and developing our resources of phosphates in the British Empire, and especially for our making the fullest use of our home resources of basic slag.

At Cockle Park, in the six years ending 1917, on the poor clay pasture of Tree Field, the untreated plot gave average annual live weight gains from sheep grazing on it of only 21¼ lbs. an acre, whereas the repeated application of high grade basic slag (39 per

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cent. phosphates) increased the average annual live weight gains to 103 lbs. an acre, or nearly fivefold. In the Hanging Leaves pasture fields, for the same six years, the average live weight gains per acre were 195 lbs. from cattle and sheep from pasture land (originally as poor as that of Tree Field), which receives a dressing of 5 cwt. an acre of high grade basic slag every third year. Three years' leys at Cockle Park, receiving one dressing of 10 cwt. an acre of high grade basic slag, gave average crops of about 42 cwt. hay an acre in each of the three years after the application of the slag. No other manure was used throughout the three years. The clover aftermaths were of a most valuable character for grazing, and as good in the second and third years as in the first. The oat crops that follow when these three years' leys are ploughed out are heavy and valuable, largely because of the good effects of the basic slag applied for the hay crops. The turnip crops which follow the oats evidently receive as much or even more benefit from the slag applied for the previous hay crops than from superphosphate applied direct to the swedes.

At Cockle Park basic slag, at about half the cost, proves a more effective manure for mangels and for beans than superphosphate.

The Guide, issued from Cockle Park annually, and other bulletins issued from that Station, give the full results of these and other trials. At that Station there is little need for the use of nitrogenous manures, because the judicious application of basic slag on the arable and pasture land stimulates clover herbage, which latter collects an abundant supply of nitrogen indirectly from the air.

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Mr. George Scott Robertson spoke on "A Comparison of the Effect of Various Types of Open Hearth Basic Slags on Grassland."

A COMPARISON OF THE EFFECT OF VARIOUS TYPES OF OPEN HEARTH BASIC SLAGS ON GRASSLAND.

By George Scott Robertson, M.Sc.

In a paper read to the Society of Chemical Industry in January, 1916,* the writer drew attention to the large quantities of open hearth basic slag then being produced on Tees-side. It was pointed out that little, if any, of this basic slag found its way on to the agricultural market, largely on account of the low solubility of the phosphate according to the then official citric acid test,† and partly, though to a much less extent, on account of the lower percentage of phosphoric acid which it contained. The low solubility of these open hearth basic slags (only 20-50 per cent. of the phosphoric acid was soluble, according to the citric acid test, compared with 80-90 per cent. of the higher grade basic Bessemer slags) was shown to be due to the fluorspar which it was necessary to introduce into the furnace during the manufacture of steel by the basic open hearth process in order to secure a readily fusible slag.

Attention was moreover directed to the fact that such open hearth basic slags were the outcome of a different process of manufacture, resulting in the production of a type of phosphate similar to that in mineral phosphates,‡ and that whatever significance the citric acid test as then practiced had, the altered conditions of manufacture entirely destroyed it.

Continuous extractions with the official citric acid solution demonstrated that the test by no manner of means gave a fair representation of the solubility of the phosphoric acid in open hearth basic slag, and cases were cited where a second extraction brought considerably more phosphoric acid into solution than was obtained in the first extraction. Even two extractions did not suffice to bring all the citric soluble phosphoric acid into solution, and it was demonstrated that if four or five half hour extractions were made, practically all the phosphoric acid in these slags could be dissolved by the weak citric acid solution.

Solution of the phosphoric acid in the soil is a continuous process, and it was argued from these laboratory experiments that the citric acid test was not a correct criterion of the agricultural value of these open hearth basic slags.

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* Journ Soc. Chem. Ind., Vol. XXXV., p. 216.

† To perform this test 5 gms. of the phosphate is placed in a litre flask containing 500 cc. of 2% citric acid solution. The flask is shaken end over end for 30 minutes in an apparatus making 30 revolutions per minute.

‡ Journ. Agric. Science, Vol. VIII. p. 1

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In order to test these deductions three field experiments were started on old grass land in Essex during the winter of 1915, and subsequently several other centres during 1916, 1917 and 1918. Three types of soil were selected, namely, the London clay, Boulder clay, and the Chalk soils. Quarter acre plots were marked off and the phosphates applied at a standard rate of 200 lbs. of phosphoric acid per acre.

The fields selected had not received artificial manures for at least twenty to thirty years previously, and since the application of the various types of phosphate, when the experiments commenced no further dressings of any description have been applied.

Chemical examination showed that all the soils save one were very deficient in total phosphoric acid, that all were deficient in available phosphoric acid, and that only one, the chalk soil, contained an adequate supply of calcium carbonate. The figures are set out below.

TABLE I.

Partial analysis of the soils at the various experimental centres.

	BOULDER CLAY.			LONDON CLAY.		CHALK.
	Tysea Hill.	Martins Hearne.	Farnham.	Latchingdon	Horndon.	Wendens
	%	%	%	%	%	%
Phosphoric acid (sol. in strong H Cl.)	.101	.089	.118	.077	.078	.210
Available Phosphoric acid	.0051	.0046	.0067	.0066	.0030	.0013
Calcium Carbonate ...	0.00	0.00	0.46	0.37	0.25	36.30
Lime requirement ...	0.29	0.27	0.00	0.05	0.00	0.00

Considerable difficulty was experienced in 1915 in securing suitable open hearth slags, as none of the steel firms approached were prepared to grind even a limited quantity for experimental purposes. Eventually an open hearth basic slag in which only 45 per cent. of the total phosphoric acid was citric soluble, was secured, and for the later experiments open hearth slags with as low solubilities as 20-30 per cent. were obtained. The collected results from these experiments are given in Table II.

An examination of the results presented in this table indicates that whilst the returns from the various open hearth basic slags are somewhat erratic when contrasted with basic slags of high citric solubility, they have nevertheless given in every case highly profitable returns. In each experiment the open hearth basic slag of 45 per cent. solubility has proved to be strictly comparable with the highest citric soluble types of basic slag. On the other hand, the open hearth basic slags with a solubility of from 20-30 per cent. do not, on the whole, do quite so well. At Martins Hearne, for example, the returns are distinctly inferior to the high citric

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soluble slag, although it must be borne in mind that the open hearth basic slag plot would be considered an excellent and highly profitable one compared with the unmanured, were it not for the contrast afforded by both the rock phosphate and the high citric soluble slag plots. (See Fig. 1.)

TABLE II.

Manures. 200 lbs. P_2O_5 per acre	Citric Solubility of the Phosphate.	Hay, Cwts. per acre.					Chalk.
		Boulder Clays.		London Clay.			
		Tysea Hill Average 4 years.	Martins Hearne Average 3 years.	Latchingdon Average 4 years.	Horndon 1 year.	Lambourne End 1 year, 1919.	Saffron Walden Average 4 years
High Grade Basic Slag	92.	30.9	—	31.7	—	—	41.2
Gafsa Rock Phosphate	38.	30.5	29.1	29.7	23.0*	25.0†	38.7
No Manure	—	20.3	16.0	21.7	15.5	13.2	31.1
Open Hearth Fluorspar Basic Slag (1)	45	32.8	—	30.8	—	—	40.0
do. do. (2)	20	—	22.7	—	18.8	26.6	—
do. do. (3)	32	—	—	—	—	16.0	—
Low Grade High Citric Sol. Basic Slag (1)	93	32.8	—	31.6	—	—	35.2
do. do. (2)	82	32.3	—	33.9	—	—	40.2
do. do. (3)	91	—	30.2	—	22.5	24.5	—
do. do. (4)	80	—	—	—	—	23.7	—
Average Rainfall, 1st May till Harvest (inches)		4.66	6.91	4.88	2.25	3.26	2.74
do. 1st April till Harvest (inches)		7.02	9.35	7.11	4.64	6.46	5.26

* Egyptian Phosphate. † Cambridge Coprolites.

A great deal of stress cannot be placed upon the one year's hay returns at Horndon. Circumstances prevented the sowing of the manures on the plots till February 27th, 1918, and as the hay crop was cut during the first week of July, the manures had not time enough to produce their maximum effect. During the 1919 season the plots were grazed at this centre by cattle and sheep, and

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the relative effect of the various types of basic slag was judged by their influence on the botanical composition of the flora.

At Lambourne two types of open hearth basic slag of very similar composition and solubility were compared with two low grade slags of high citric solubility. The experiment has as yet only been running for one year, but as the response to phosphates during the dry season of 1919 is very marked, the results are not without significance. An open hearth slag plot is always next to a high citric soluble slag plot, so that the risk of soil variations interfering with the results has been reduced to a minimum. Open hearth basic slag 2 is next to high citric soluble slag 3, and it will be seen that open hearth basic slag 2 gives slightly superior results. On the other hand, however, open hearth basic slag 3 and high citric soluble basic slag 4 are also next to each other, but in this case the high citric soluble slag is much superior. Open hearth basic slag 3 shows a very poor return for the first year at any rate.

On soils well supplied with calcium carbonate, the low citric soluble phosphates do as well as the high citric soluble basic slags in the wetter seasons, but they do not do so well during the drier seasons. On acid soils low citric soluble phosphates appear to do quite as well as the high citric soluble phosphates in dry and in wet seasons.

It is not infrequently remarked by farmers that the basic slag of to-day is not so good as the " old slag." In the writer's experience, however, this opinion is largely due to it not being sufficiently realised that the " new " open hearth basic slags contain only from 18-26 per cent of phosphate, compared with 36-44 per cent. in the high grade basic Bessemer slags. Many farmers, when applying basic slag, pay little attention to its phosphate content, and work on the principle of applying 3-5 cwt. for a cereal or root crop and 5-7 cwts. on a meadow, irrespective in many cases of the grade of the slag.

Effect of Open Hearth Basic Slag on Pastures.

The great value of basic slag on pastures is largely due to its effect in encouraging the growth of clovers, particularly wild white clover. On the heavier soils poor pastures, consisting chiefly of coarse grasses and weeds without any visible signs of clover, may in the course of a year to eighteen months be transformed into first class pastures covered with a luxuriant bottom of wild white clover as a result of a liberal dressing of phosphoric acid in the form of basic slag. Wild white clover is a bottom clover, and it seldom gets into the hay cut in Essex. For this reason, therefore, the increased weight of hay is not an adequate measure of the improvement produced by the application of slag. Whilst the hay crop may be doubled on the slag plots, feeding trials would in all probability show from three to six times greater returns on the slagged plots than on the unmanured.* Unfortunately, with the facilities available it has not been possible to conduct grazing trials. The plots on two of the experimental centres have, however, been grazed with

* Guide to Cockle Park, 1917 page 14.

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cattle and sheep at Farnham for two seasons and at Horndon for one season. During August and September, 1919, determinations of the area occupied by the various types of vegetation were made by the method recommended by Armstrong.* The results are set out in the following tables:—

TABLE III.

Type of Vegetation.	Farnham (Boulder Clay Soil).			Horndon (London Clay Soil).		
	Plot 1. Open hearth Basic Slag (Solubility 20%).	Plot 2. High Citric Soluble Basic Slag (Solubility 91%).	Plot 3. No Manure.	Plot 18. Open hearth Basic Slag (Solubility 20%).	Plot 17. High Citric Soluble Basic Slag (Solubility 91%).	Plot 16. No Manure.
	%	%	%	%	%	%
Clovers ...	27.1	50.2	16.2	43.8	46.2	9.4
Grasses ...	45.0	33.3	18.4	31.8	47.2	19 1
Weeds ...	16.0	13.5	25.0	13.3	1.4	26.0
Bare Space	11.9	3.0	40.4	11.1	5.2	45 5
	Manures sown Feb. 22nd. 1917.			Manures sown Feb. 27th, 1918.		

There can be no doubt from a study of Table III. and Fig. 2 that at both centres the application of open hearth basic slag has resulted in a marked improvement in the pasture—and one which is much greater than might have been expected from the low citric solubility of the slag. At neither centre does the open hearth basic slag do quite so well as the high citric soluble basic slag. At Horndon, where the soil is exceptionally poor in total and available phosphoric acid, the difference between the two types of basic slag is not great. At Farnham, where the content of total and available phosphoric acid in the soil is considerably higher, the differences between the two types of slag are more marked. The superior results from the high citric soluble slag at Farnham are largely due to the more even growth of the clover and the absence of comparatively bare spots in this plot. On the open hearth basic slag plot, the clover bottom is less regular and is not so close.

The Relation of Citric Solubility to the Value of the Phosphate.

At Tysea Hill, Latchingdon, and Horndon, there appears to be little or no relation between citric solubility and the increase in hay crop or the improvement of the pasture. At Martins Hearne and Farnham, on the other hand, solubility is of some importance, though in neither case does the citric acid test appear to give a fair or reliable indication of the relative value of the two types of basic slag. The results from the Lambourne experimental centre are more difficult to interpret. An open hearth basic slag of very low solubility, 20 per cent., gives the best results, whilst another of somewhat higher solubility, 32 per cent., gives the poorest results.

* Journ. Agricult. Science, Vol. II., p. 286.

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It is not a question of a difference of a hundredweight or so of hay, but of 10 cwts., or, interpreted in percentages, one open hearth slag gives an increase in the hay crop of slightly over 100 per cent., whilst the other only increases the crop slightly over 20 per cent.

It is difficult to resist the conclusion that there is a great difference in the rate at which the phosphoric acid in these two open

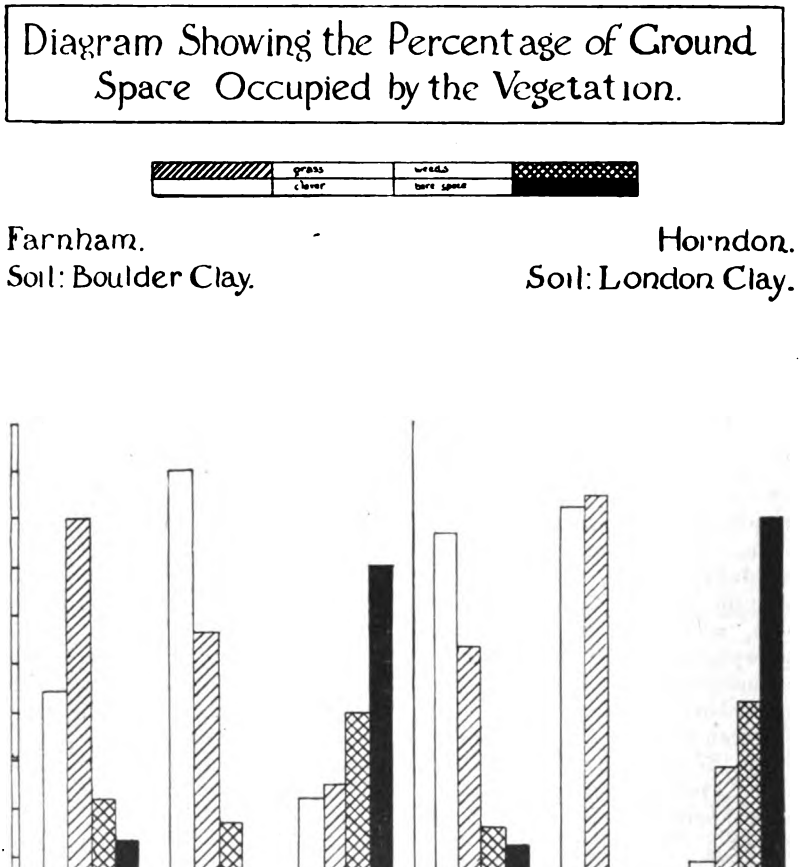

FIG. 2.

hearth slags is rendered available for the plant in the soil. In order to ascertain whether any difference between various open hearth basic slags could be brought out in the laboratory by solution in citric acid, a series of solubility trials were made, using one gramme of slag instead of five, and keeping the remainder of the conditions

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precisely the same as in the official test. In the following table the results for a variety of phosphates are set out and compared with the solubilities according to the old official citric acid test.

TABLE IV.

Description of Phosphate.	Total P_2O_5 %	Citric Soluble P_2O_5 5 gms. %	Citric Soluble P_2O_5 1 gm. %	Citric Solubility per cent.	
				Using 5 gms.	Using 1 gm.
High Grade Basic Slag (1)	17.84	16.40	16.93	92.0	94.9
do. do. (2)	17.08	15.42	17.12	90.3	100.0
Low Grade High Citric Soluble Basic Slag ... (1)	11.50	10.75	11.18	93.4	97.2
do. do. (2)	9.69	7.99	8.92	82.2	91.0
do. do. (3)	12.91	11.78	12.96	91.2	100.0
do. do. (4)	9.98	8.00	—	80.2	—
Open Hearth Basic Slag (1)	12.40	5.68	8.44	45.0	68.0
do. do. (2)	11.74	2.36	7.12	20.1	60.6
do. do. (3)	9.10	2.93	3.43	32.2	37.7
do. do. (4)	9.20	1.61	1.68	17.5	18.3
do. do. (5)	10.97	3.75	4.85	34.2	44.3
Gafsa Rock Phosphate ...	26.21	10.05	23.36	38.3	89.1
Egyptian Phosphate ...	26.72	9.28	21.13	34.7	78.2
Algerian Phosphate ...	29.32	9.79	24.22	33.4	82.6
Tunisian Phosphate ...	24.95	5.95	18.18	23.9	72.9
Florida Pebble Rock Phosphate	33.19	6.06	20.88	18.2	62.6
Apatite	39.49	1.28	4.16	3.2	10.5

The above table brings out several points of considerable interest. The solubility of high grade basic slags are, as might be expected, not greatly affected by modifying the test, so that one gramme instead of five is shaken for half an hour with 500 c.c. of 2 per cent. citric acid.

The figures for open hearth basic slags and the various rock phosphates afford a striking contrast. Gafsa rock phosphate has now a high percentage solubility, comparable with that of a high grade basic slag, instead of a low one, and it is worthy of note that in the field trials Gafsa rock phosphate proves to be approximately equal to the higher grades of basic slag. The same holds true to a lesser extent with the other types of rock phosphates.

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The modified test brings out some curious differences between the various open hearth basic slags. Open hearth basic slags 1 and 2 show a much greater solubility by the modified method; Nos. 3 and 4, on the other hand, are little affected by the change. Moreover, it is 1 and 2 which do so well in the field trials, whilst No. 3 does badly (see results from Lambourne, Table II).

For the one experimental centre, Martins Hearne, where solubility appears to be of some importance, the average field returns

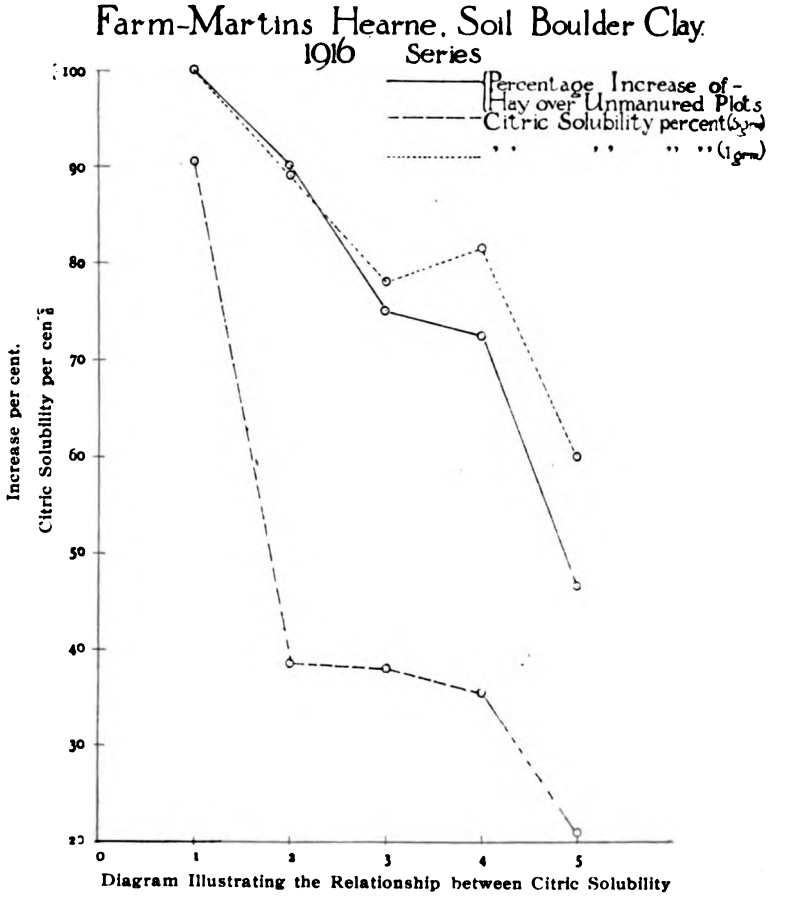

Diagram Illustrating the Relationship between Citric Solubility and Increase of Crops.

FIG. 3.

from the various phosphates over a period of three years, the solubility of the phosphates, according to the former official citric acid test, and when 1 gramme is used in performing the test instead of 5, are shown graphically in Fig. 3. The high citric soluble basic slag gave an average increase of 90 per cent. over the unmanured plot. This increase has been taken as 100, and the percentage increase for the other phosphates modified accordingly. Reference to Fig. 3 shows little or no correlation between the field returns and

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the solubilities of the phosphates according to the old official citric acid test, but there is, on the other hand, a fairly close relationship between the field returns and the solubilities when 1 gramme instead of 5 grammes is used in performing the test.

It is not suggested that these results justify the setting up of a new citric acid test. The field trials do, however, show considerable differences in the returns from open hearth basic slags, which have every appearance of being similar. These differences are not brought out by the old official test; in fact, they are sometimes disguised; compare results in Table IV from open hearth basic slags 2, 3, 4, and 5. The modified method does serve to distinguish between these slags.

The information from the field trials is somewhat limited, and it would seem, in view of the facts brought out, very desirable that a number of these open hearth basic slags should be tried at two or three experimental centres where the phosphoric acid content of the soil is low, and the response to phosphatic manuring consequently pronounced.

The Utilisation of the Lower Grades of Open Hearth Basic Slag.

The majority of the open hearth basic slags at present on the agricultural market contain from 9 to 12 per cent. of phosphoric acid. There are, however, very large quantities of these slags containing from 5 to 8 per cent. of phosphoric acid, which present conditions make it difficult to market because grinding and freight charges make their cost excessive. At the same time there is a scarcity of phosphates, and the demand by the agricultural community is increasing at a greater rate than supplies are becoming available. If the phosphoric acid content of these lower grade open hearth basic slags could be raised to a level of 10 per cent., it would be possible to market them and thus to no inconsiderable degree relieve the existing shortage. The use of rock phosphates for this purpose has been suggested by Professor Gilchrist, and even prior to 1914 was successfully carried out by several manufacturers. The desirability of such a method of grading up these open hearth basic slags turns upon the extent to which these rock phosphates are comparable with the phosphates in basic slag. Professor Gilchrist's results at Cockle Park,* Professor Hendricks' in Aberdeen, and the writer's results in Essex show that they are but little inferior as a source of phosphoric acid to the higher grades of basic slag. An indication of the Essex results from various rock phosphates is given in Table II by the returns from Gafsa rock phosphate, but they will be dealt with in more detail at a later period. They suffice to show, however, that rock phosphates as a source of phosphoric acid are quite equal, if not superior to open hearth basic slag, so that no objection could be taken to them from this point of view.

There are three ways in which rock phosphates could be used for this purpose:—

1. By addition to the furnace.
2. By addition to the molten slag in the ladle.
3. By grinding and mixing with the ground slag.

* Guide to Cockle Park, 1917, page 34.

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Of the three methods the first is undesirable, as it entails an alteration in the furnace charge, whilst the third method involves two separate grindings if the mixing is to be thorough. The second method avoids the disadvantages of the other two, and is the easiest to manipulate and control.

Conclusions.

1. The field trials indicate that open hearth basic slags provide a valuable source of phosphoric acid on soils very deficient in this ingredient, and that these slags can be very profitably used for the improvement of our heavy clay soil pastures and meadows.

2. The laboratory and field results both suggest that open hearth basic slag is not a uniform material, and that important differences may exist between two open hearth basic slags of similar solubility. One may succeed, whilst the other produces poor results.

3. Solubility according to the citric acid test is no criterion nor yet an approximate indication of the fertilising value of open hearth basic slags compared with high citric soluble basic slags.

4. It is eminently desirable that several series of field experiments on both arable and grass-land should be carried out over a period of years with as many different types of open hearth basic slags as can be conveniently procured. It cannot be too often emphasised that they contain a new type of phosphate, and much more information than at presents exists is necessary, as well as desirable.

5. It has often been stated that the foundation of a permanent system of soil fertility depends more than anything else upon an adequate supply of phosphates. In view, therefore, of the increasing agricultural demand for phosphates, it is advisable that consideration should be given to the feasibility of grading up the phosphoric acid content of the lower grades of open hearth basic slags in such a way that it may be economically possible to place them on the agricultural market.

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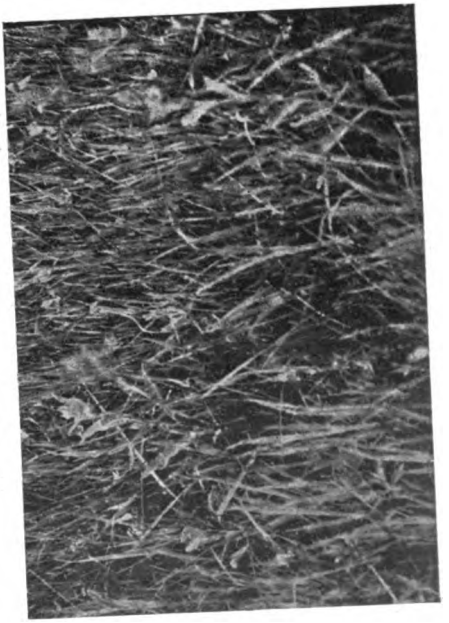
MARTINS HEARNE.
SOIL :—BOULDER CLAY.

PLOT 2—Low Grade High Citric Soluble Basic Slag (91% Citric Soluble).

PLOT 4.—Gafsa Rock Phosphates (38% Citric Soluble).

PLOT 1.—Open Hearth Basic Slag (20% Citric Soluble).



PLOT 3.—No Manure.

FIG 1.
(Photographs taken June, 1918.)

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The following papers on "Solubility of Basic Slags" were presented by **Dr. J. E. Stead, Mr. F. Bainbridge and Mr. E. W. Jackson.**

SOLUBILITY OF BASIC SLAGS.

Part I.—The reason why fluorspar in Basic Slags reduces the solubility.

By F. BAINBRIDGE.

Part II.—On the solubility of Basic Slags in citric acid and water solutions of carbonic acid.

By J. E. STEAD, D.Sc., F.R.S., and E. W. JACKSON, F.I.C.

PART I.

THE REASON WHY FLUORSPAR IN BASIC SLAG MAKES IT RELATIVELY INSOLUBLE.

By F. BAINBRIDGE, Skinningrove.

The present note is given by permission of the Council of the Iron and Steel Institute.

It has long been known that the use of fluorspar in the manufacture of steel by the basic open hearth process has brought about a remarkable reduction in the citric acid solubility of the slag produced.

During the past two years the author has been engaged upon a research on the above subject which will shortly be presented to the Iron and Steel Institute in the form of a Carnegie Scholarship Memoir, and it was thought that a short summary of part of the work carried out would be of interest to those taking part in the present discussion.

A.—Fusions were made consisting of a citric soluble slag and varying quantities of calcium fluoride, and a curve of the solubility values plotted. By this means it has been shown that the solubility of the phosphate decreases rapidly, until a calcium fluoride to tri-

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calcic phosphate ratio of about 8 to 100 is reached. After which the soluble to total phosphoric acid ratio becomes approximately constant.

B.—Fusions of pure tricalcic phosphate and also synthetic compounds approximating to the formulae $4CaO.P_2O_5$ and $3CaO.P_2O_5.2CaO.SiO_2$ were then made with the addition of varying amounts of calcium fluoride, and it was found that in all cases the solubility of the phosphates followed a curve similar to that above mentioned. It was also found that the extra lime in the first and the calcium silicate in the second of the two synthetic compounds remained almost completely soluble, although the phosphoric acid solubility was reduced considerably. This would indicate the formation of a new compound consisting of lime, phosphoric acid and calcium fluoride, with liberation of lime and dicalcic silicate respectively.

C.—A slag was then made in the basic open hearth furnace with large additions of calcium fluoride, about 8 tons run off into a ladle and allowed to cool slowly for four days. On breaking open the slag the central portion was found to be filled with a large mass of clear needle crystals of a slightly brownish tint, together with some quantity of dark grey material, part of which, under the microscope, showed a very distinct fern-like structure. A quantity of the crystals was collected, and practically the whole of the grey material separated with an electromagnet. A portion of the needle crystals was ground, again separated with the magnet, the magnetic portion rejected, and the remainder subjected to analysis.

	%
Silica	1.10
Alumina	nil
Iron expressed as peroxide	0.57
Manganous oxide	0.14
Lime and calcium fluoride expressed as calcium oxide	56.30
Phosphoric acid	37.39
*Fluorine	6.50
Vanadic oxide	nil
Chromic oxide	nil
Magnesium oxide	trace

This analysis may be summated as follows:—

Apatite 3 ($3CaO.P_2O_5$) CaF_2	88.47
Excess calcium fluoride	6.50
Dicalcic silicate	3.15
Impurities, Fe_2O_3 and MnO, &c.	1.88

These crystals have been examined by Mr. A. F. Hallimond, of the Geological Survey, and Mr. L. J. Spencer, Mineral Dept., Natural History Section, British Museum, and both these gentlemen are satisfied that the crystals are artificial apatite in hexagonal prisms, although no terminal faces have been obtained. Mr. Spencer, however, states that he has been able to make some

* Fluorine determination in slag pre ents many difficulties and the above figure is an average of results by several analytical methods and it is hoped to have this figure confirmed shortly by an independent analyst.

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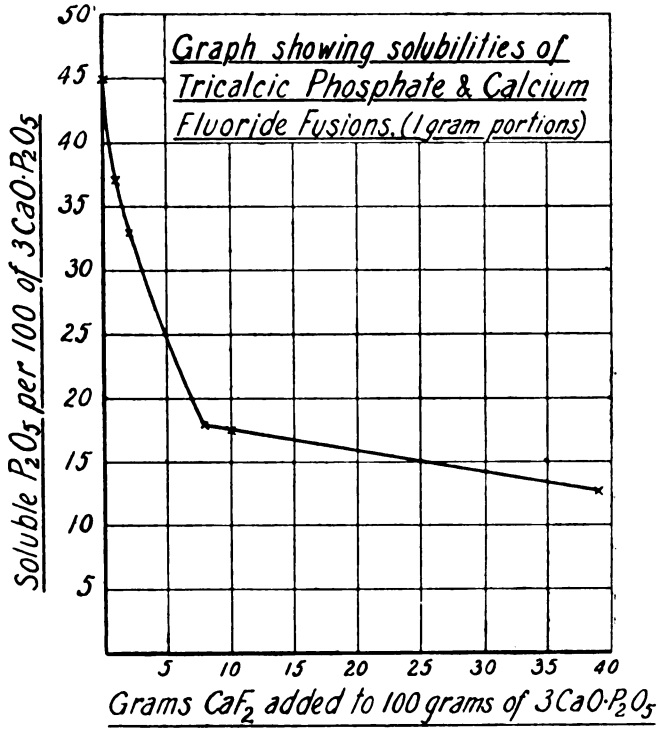
accurate determinations of the refractive indices in sodium light through clear prisms.

On washing the crushed crystals with cold 2 per cent. solution of hydrochloric acid, it was found that the bulk of the dicalcic silicate was removed, leaving the apatite and free calcium fluoride insoluble, together with the iron and manganous oxides.

A citric acid solubility test on a five gram portion of the unwashed crystals showed 2.04 per cent. soluble phosphoric acid, which is equal to 5.45 parts soluble phosphoric acid per 100 parts total phosphoric acid, or 2.50 parts of soluble phosphoric acid per 100



parts of tricalcic phosphate. One gram of the crystals ground to a flour in an agate mortar and treated with 500 c.c. of 2 per cent. citric acid solution for half and hour at 40 revolutions per minute showed 9.82 per cent. soluble phosphoric acid, which is equal to 26.26 parts of soluble phosphoric acid per 100 parts of total phosphoric acid, or 12.03 parts of soluble phosphoric acid per 100 parts of tricalcic phosphate.

For comparison a curve is given below showing the solubilities of one gram portions of fusions of tricalcic phosphate with varying amounts of calcium fluoride, ground to a flour and treated with 500 c.c. of a 2 per cent. citric acid solution, as in the case of the crystals.

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The magnetic material, after careful crushing and magnetic separation, gave the following analysis:—

	%
Silica	1.30
Alumina	1.84
Ferric oxide	23.29
Ferrous oxide	26.23
Manganous oxide	14.04
Lime	7.40
Magnesia	24.94
Phosphoric acid	1.03

This material, being somewhat similar to that described by Stead and Ridsdale in a paper before the Iron and Steel Institute in 1887, the principal difference being that the material examined by them contains more lime and less magnesia than the above.

PART II.

NOTE ON THE SOLUBILITY OF BASIC SLAG IN CITRIC ACID AND CO_2 SOLVENT.

By J. E. Stead, D.Sc., F.R.S., and E. W. Jackson, F.I.C.

From time to time the question has arisen of the possibility of using CO_2 solvent for the determination of the soluble phosphoric acid in basic slags.

In 1895, Stead* discussed the question of solubility of basic slag of varying composition, and other phosphates, both in acid citrate of ammonium solution, and carbonic acid water.

The slags experimented on were all pounded to the fineness of flour, and were not in the somewhat coarser condition, or what goes through the 100 × 100 sieve.

The citrate solution was different from that generally used to-day —2 per cent. citric acid in water—but was the one prescribed by Wagner at the time, and contained per litre 100 grams citric acid neutralised by ammonia and 10 grams excess of citric acid added. It contained therefore 10 per cent. citric as ammonium citrate, and 1 per cent. of free citric acid.

The carbonic acid water solvent made at a soda water manufactory was supplied in pint bottles, which contained about 580 c.c. solution. The stoppers were removed to allow the excess of CO_2 to escape, the slag powders introduced, and the stoppers replaced. The bottles with powders were allowed to stand for 24 hours, and the liquid examined for phosphoric acid.

The quantity of slag powders used was very small, only 0.1 grams.

In determining the acid citrate solubility, one part each of the fine powders was placed in the bottom of glass beakers and 100 parts by volume of citrate solution was poured on them.

* Stead, Proc. Cleveland Institution of Engineers, 1895.

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The contents were agitated for one hour, and were then allowed to rest for 20 hours. The following are a few of the results obtained by the two methods.

TABLE I.

	P_2O_5 %	SiO_2 %	Parts per 100 P_2O_5 dissolved By Acid Citrate. %	By Carbonic Acid 20 hours. %	½ hour
1st basic slag	7	16.8	100	100	—
2nd basic slag	11.37	15.6	100	94	—
3rd basic slag	17.00	9.0	97	70	—
4th basic slag	23.6	6.5	69	69	—
5th basic slag	19.0	8.8	67	47	—
Belgian phosphates ...	25.4	0.9	33	20	—
Brown Hexagonal crystals	19.0	2.0	33	—	—
Blue silico phosphate crystals ...	25.36	11.2	99.8	85.00	46.0
Tabular plates of tetra-basic phosphate of lime ...	33.0	1.5	34.0	14.60	—
Apatite ...	—	—	7.0	—	0.41

The results obtained indicate that for normal basic slags the solubility increases with the amount of silica present, and also indicate how insoluble natural apatite is, in either citric or carbonic acid.

Similar trials have been made by C. G. T. Morison.* The material experimented on did not, however, vary to any great extent in citrate solubility.

The authors thought it desirable to experiment on material of more variable solubility.

For the purpose of this paper Mr. E. W. Jackson, Dr. Stead's head assistant, has made experiments on a series of basic slags varying in citrate solubility. They were in powder of standard fineness, except in the case of the slag, which contained the phosphate entirely in the state described by Mr. Bainbridge as artificial apatite.

The slags A, B, and C are those with which Mr. Bainbridge made pot trials to determine their agricultural value in growing barley (Carnegie Scholarship Research Memoirs, 1919).

The samples may be described as follows:—

A.—Soluble slag. Made without the addition of fluorspar.

B.—Insoluble slag. Made with considerable addition of fluorspar.

C.—Partly soluble slag. Made with small addition of fluorspar.

D.—Crude apatite crystals taken from a slowly cooled basic slag (referred to by Bainbridge).

A, B, and C were pounded until all the sample passed through a 100 × 100 sieve.

* C. G. T. Morison, *Journal of Agriculture*, 1909.

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The composition of the four samples as to total P_2O_5 and P_2O_5 soluble in 500 c.c. 2 per cent. citric acid solution on 5 grams of the powders were as follows:—

TABLE II.

	A.	B.	C.	D.
	%	%	%	%
Total P_2O_5 ...	14.50	14.10	12.60	27.00
Soluble P_2O_5 ...	10.50	0.87	3.28	1.21
Percentage solubility	72.5	6.2	26.0	4.5

Bainbridge, it will be noticed, found in D sample a citrate solubility of 5.45 per cent., and in the dead fine powder 26.26 per cent., or an increase of more than 20 per cent.

Analysis of Sample D.

	%
Silica	4.20
Lime	50.00
Phosphoric acid	27.00
Oxide of iron	7.00
Oxide of manganese	2.00
Alumina	trace
Magnesia	3.50
Fluorine (by difference)	6.30
	100.00

For the solubility in CO_2 solvent, D sample was pounded to great fineness in an agate mortar.

The conditions under which the experiments were carried out were as follows:—

Using CO_2 water as solvent.

(A).—Half gram portions of each sample were placed in ordinary soda water bottles containing 280-285 c.c. of CO_2 solvent (instead of twice as much as previously used by Stead).

The bottles had been filled previously at a mineral water factory, and contained about 3.5 vols. CO_2.

The stoppers were removed, and after the first violent evolution of gas the weighed portions of the slag powders were dropped into the bottles, which were rapidly restoppered and allowed to lie on their sides, with occasional shaking for 24 hours.

After filtration and washing with cold water (free from CO_2) the filtrate was tested for P_2O_5, and the insoluble treated exactly as before with a fresh quantity of CO_2 solvent, the process being repeated until no more P_2O_5 was dissolved out.

The results obtained on each 24 hour test are shown below, the 2 per cent citric acid solubilities being inserted for comparison.

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TABLE III.

Solubility in CO_2 solvent.	Phosphoric Acid per cent. A	B	C	D
After 1st day	4.77	0.54	1.34	1.07
After 2nd day	3.58	0.21	0.34	1.04
After 3rd day	1.01	0.12	0.11	0.11
*After 4th day	0.37	trace	trace	trace
After 5th day	0.15	nil	nil	nil
After 6th day	trace	nil	nil	nil
Total Solubility	9.88	0.87	1.79	2.22
Parts per 100 P_2O_5	66.0	6.2	14.2	8.0
2% citric acid solubility ...	10.50	0.87	3.28	1.21
Parts per 100 P_2O_5	72.5	6.20	26.0	4.5

(B).—Another half gram portion of each slag powder was added to the CO_2 solvent in the same way, and, after being stoppered, was placed in an end-over-end shaking machine, which was rotated at 40 revolutions per minute for 30 minutes.

At the end of that period the samples were removed from the machine and treated as in the previous case, the insoluble remaining being rotated again under the same conditions, the treatment being repeated until no further soluble P_2O_5 was obtained. The results were as follows:—

TABLE IV.

Solubility in CO solvent.	Phosphoric Acid per cent. A.	B.	D.
1st shaking	4.40	0.67	2.80
2nd shaking	1.79	0.18	0.45
3rd shaking	1.37	0.07	0.13
*4th shaking	0.90	nil	0.07
5th shaking	1.56	nil	trace
6th shaking	0.37	nil	nil
7th shaking	0.19	—	—
8th shaking	trace	—	—
9th shaking	nil	—	—
Total dissolved on 100 parts P_2O_5	10.58	0.92	3.45
	73.0	7.2	12.7
2% citric acid solubility ...	10.50	0.87	1.21
On 100 parts P_2O_5	72.5	6.2	4.50

* Between the 4th and 5th shaking the sample was left in the solvent over the week-end, which probably accounts for the higher result.

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(C).—A further half gram portion of each was allowed to stand 6 days with occasional shaking. The results were:—

	A.	B.	C.	D.
Soluble P_2O_5	8.95	0.93	1.79	2.12
On 100 parts P_2O_5	61.7	7.3	14.2	7.80
After other three days—				
Soluble P_2O_5	0.90	trace	trace	0.41
On 100 parts P_2O_5 on original slag	68.0	7.3	14.2	9.4
And after a further 2 days—				
	0.25	nil	nil	0.11
Total solubility	10.10	0.93	1.79	2.64
On 100 parts P_2O_5	70.0	7.3	1.42	9.8

Summary of Results.

TABLE V.

	Citric Acid %	Carbonic Acid Series. A. %	B. %	C. %
A	72.5 ...	66.0	7.3	70.0
B	6.2 ...	6.2	7.2	7.3
C	26.0 ...	14.2	spoilt	14.2
D	4.5 ...	8.0	12.7	9.8

It will be noticed that in the cases A, B, and D long continued attack by carbonic acid dissolves out as much or more phosphoric acid than the single attack by the standard citric acid.

The exception is in sample C, in which only about half the amount is dissolved out by the CO_2, as by citric acid for reasons which are not at present known.

Conclusions.

The reason why fluorspar makes the phosphoric acid in basic slag relatively insoluble is because the fluoride unites with the phosphate of lime and produces artificial apatite, which, as regards insolubility, resembles natural fluorapatite.

As calcium chloride has the same effect as fluorspar, it may be assumed that chlor-apatite is formed, which is also insoluble.

The most soluble slags, which yield the double salt of tri-basic phosphate and silicate of lime, are made insoluble on melting them with fluorspar.

It has been proved that the finer the powder, the more phosphoric acid is dissolved out of the insoluble slags by citric acid, and on the same material long continued attack by carbonic acid generally dissolves out more phosphoric acid than a single attack by the standard citric method.

As a rule, the more insoluble a slag, the less readily is the phosphoric acid dissolved out of it by either solvent.

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DISCUSSION.

Mr. Norman Sheldon, A.R.C.S., A.I.C.

(Communicated contribution to the discussion on the paper by DR. J. E. STEAD, MR. F. BAINBRIDGE *and* MR. E. W. JACKSON.

I have read this paper with much interest, as I have been working on basic slags for the last twelve months, and had arrived at the same conclusion as Mr. Bainbridge with regard to the formation of fluorapatite in slags to which fluorspar had been added.

The slags with which I have been working are low grade slags containing about 7 per cent. of P_2O_5. Tiny crystals were observed in many odd specimens of slag, and I decided to try to obtain larger crystals in order to examine them carefully.

A slag was cooled slowly in order that crystals might have every chance of developing. On examination it was found that crystals appeared to a considerable extent, and it was possible to distinguish several varieties.

Three distinct sets of crystals were obtained:—

(i) Colourless hexagonal needles.

(ii) Yellowish brown hexagonal plates.

(iii) A black magnetic body with a tendency to fernlike formation.

Owing to the low percentage of P_2O_5 (6.5 per cent.) in the slag, the crystals were very small, and it was impossible to detach them completely from the main body of the slag in sufficient quantity to analyse.

The colourless needles (i) were examined under the microscope and resembled apatite in appearance. When treated with sulphuric acid under the microscope, tiny bubbles of gas were evolved in large numbers over the whole surface of the crystals, and in one case an etching action on the glass of the slide was obtained, showing that *fluorine* was present.

Crystals No. (ii) hexagonal plates, were rare, but quite distinct. The surface was often marked with a peculiar black structure resembling the black magnetic body (iii), and probably was identical with that body.

Crystals (i) and (iii) are frequently found intimately mixed. The colourless needles are often found apart from the magnetic body, but the magnetic body is rarely found free from the colourless needles.

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An estimation of P_2O_5 on the crude colourless crystals free from magnetic body but *not* free from slag, showed a high percentage of P_2O_5—thus showing that the needles were a phosphate. There is little doubt that these are crystals of fluorapatite.

With regard to the determination of fluorine in slags I wish to say that I have found it impossible to determine it accurately in the small quantity in which it is present. With slags containing only .25 to 1.0 per cent. of fluorine there is no reliable method that will distinguish between such quantities as .25 per cent., .3 per cent., .35 per cent., etc.

In addition to the three classes of crystals mentioned, a fourth body was observed to be present in very small quantity when examined under the microscope. This consisted of sharply angular, transparent brown pieces resembling in many ways fragments of glass; it did not show any definite crystalline structure.

I now come to the second part of the paper by Dr. Stead and Mr. Jackson. I believe that the citric solubility test does not indicate the agricultural value of the phosphate of slags. In some cases it may do so undoubtedly, if the phosphate is soluble, no doubt it is sure to be of good value, but if it is largely insoluble it is not necessarily of very little value.

The citric acid test does not represent the conditions in the soil. The carbonic acid water test is nearer to the soil condition, but also agrees with the soil action in being very slow, and is therefore hardly a practical test. It has been shown by Mr. Bainbridge in his Carnegie Scholarship Memoir that the insoluble phosphate of slag has an agricultural value. I attribute this largely to the fact that the phosphate is in a very fine state of division in the slag; it might almost be correct to say that it is in a precipitated form when the slag is cooled relatively quickly.

Coming now to a point regarding which there has been much neglect and uncertainty, I wish to refer to the lime value of basic slag. The value of the lime in basic slag has always been recognised to a limited extent, but it is usually looked upon as a secondary consideration.

I am at present engaged on a long series of experiments regarding the solubility and therefore to availability of the lime, and I hope to bring forward evidence (of a purely chemical nature) that basic slags very low in phosphorus still have an important agricultural value apart from the presence of phosphate, and that they can take the place of lime and more particularly of ground limestone in agriculture.

A very thorough investigation into the constitution of basic slags is urgently needed from the point of view of the steel maker as well as to ascertain the commercial value of the various grades of slag. The basic process is an extremely interesting chemical process about which really very little is known. A better understanding of the chemical side of the question must undoubtedly lead to increased production and output.

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The Iron and Steel Institute Journal and other journals publish annually volumes of research almost entirely devoted to iron and steel studied chiefly from the physical and mechanical standpoint.

Such subjects as basic slag are usually dismissed with a page or so of abstracts from foreign journals.

English steel makers as a whole have been content to neglect the many problems which steel making presents to the chemist for solution.

Mr. F. Bainbridge.

(*Communicated reply to* MR. N. SHELDON.)

I am pleased to hear that Mr. Sheldon agrees as to the formation of fluorapatite in slags to which fluorspar has been added, and must thank him for the interesting data on low grade slags.

With regard to the crystals obtained, the colourless needles (i) appear to be identical with apatite, and the black body (iii) similar to that described at the end of the paper.

The yellowish brown hexagonal plates (ii) are extremely interesting, and I should be glad to hear whether Mr. Sheldon has attempted to procure sufficient of this material for analysis by allowing the slag to cool slowly in a ladle without disturbance. Also, has Mr. Sheldon any idea as to the approximate fluoride addition to the slag in which these crystals occur, as I have not seen any sign of this material in any slags containing sufficient calcium fluoride to convert all the phosphate into apatite, and it is possible that these yellow hexagonal tablets are similar to those obtained by Ridsdale (1887), and are the original unconverted phosphate.

The fourth substance that Mr. Sheldon refers to as a brown body, I believe to be a silicate possibly of the type $2CaO.SiO_2$, and under the microscope appears to have solidified after the apatite and grey fern crystals.

With regard to the free CaO content of a slag I have only come in contact with slags of higher P_2O_5 content than those with which Mr. Sheldon has dealt, and have found less than 2 per cent. free CaO with a P_2O_5 content of 14 per cent. or thereabout. I believe that this matter is of such importance as to warrant thorough investigation.

I am in agreement with Mr. Sheldon with regard to the distribution of the magnetic material throughout the mass, and also with regard to the accurate determination of fluorine in slags, and am at present engaged in an investigation of the subject.

Mr. D. Sillars: Two photo micrographs at 75 diameters are shown which appear to confirm the view of Mr. Bainbridge that the insoluble form of phosphoric acid compound in open hearth slags is fluorapatite. No. 1, to which no fluorspar was added, contains 18.65 per cent. P_2O_5, of which 14.98 per cent. = 80.26 per cent. of the total, was soluble in 2 per cent. citric acid. The structure shows

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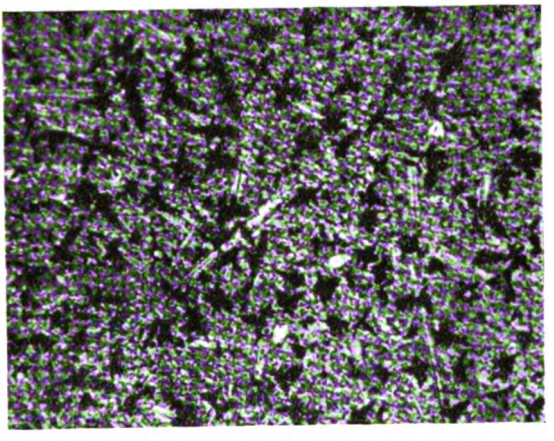
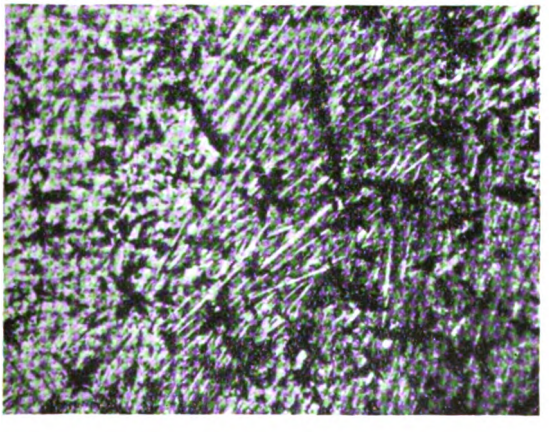
comparatively little of the columnar shaped mineral characteristic of apatite, while No. 2, to which 1 per cent. fluorspar = .65 per cent. calcium fluoride was added, shows these columns very markedly. The latter contains 20.4 per cent. P_2O_5 with 8.18 per cent. = 40.09 per cent. of the total P_2O_5 soluble in 2 per cent. citric acid. The



No. 1 × 75 dia.
Without Fluorspar.



No. 2 × 75 dia.
With 1 per cent. Fluorspar.

samples from which these sections were prepared were taken together and the fluorspar added to No. 2 in the sample pot.

Mr. Bainbridge is to be congratulated on the beautiful specimens of crystals of apatite exhibited in support of his argument.

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Mr. Hugh Richardson contributed the following remarks in a letter communicated to Sir Daniel Hall:

There is some very interesting research work in the hands of M. W. Fodor, now in Budapest, formerly works chemist to some large iron works in Lincolnshire.

He seems to have isolated from basic slag some four separate *silico-phosphates of calcium*. This may afford an explanation of the very curious difficulties in getting any satisfactory method of mercantile analysis for basic slag.

Fodor has formulae for these substances, and has examined properties of them. His work suggests a kind of parallel to Van't Hoff's investigations on the crystallisation of Stassfurt salts Mg, K, Cl, SO_4 compounds; but the equilibrium conditions of crystallisation for the silico-phosphates being at much higher temperatures.

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Mr. Daniel Sillars read a paper on "The Formation of Basic Slag in the Manufacture of Steel."

FORMATION OF BASIC SLAG IN THE MANUFACTURE OF STEEL.

By Daniel Sillars.

This contribution to the discussion on basic slag does not deal with its merits as a fertilizer, but is intended to be a brief account of the formation of the slag in the manufacture of steel.

There does not appear to be any necessary connection between agriculture and iron, other than the dependence which the latter industry shares with every other activity of man on the most ancient of all arts. During the past 50 years, however, a closer link has been established between these industries in their more highly developed forms. Scientific farming has demanded the artificial replacement of plant foods, of which the soil has become denuded, and the iron industry has been able, as a result of its own improvements in manufacture, to provide plant foods from its waste products. Nitrogen is recovered as sulphate of ammonia from blast-furnaces using raw coal and from the ovens of those furnaces which use coke, phosphorus is recovered in the slag from the steel furnace, and under the stress of war it was in the iron industry that the farmer found assistance in mitigating the effects of the shortage of potassium compounds. Although these links of interest are coincident rather than inherent, they explain the desirability of bringing about an understanding between the agriculturist and the steel maker, of the conditions under which these industries operate.

The presence of phosphorus in steel, except in very small amounts, renders it brittle and unfit for use in structures and machinery. The iron ores of Great Britain are in the main highly phosphoric, and are consequently unsuitable for the manufacture of pig iron for steel-making unless the phosphorus can be removed during the smelting operations. Attempts to remove the phosphorus from the iron in the blast-furnace have not met with any success, on account of the highly reducing conditions which exist in the hearth of the blast-furnace and which are a necessary condition of the recovery of the iron from the ore.

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Experiments by Snelus in 1872, and at Blaenavon in 1878 by Thomas and Gilchrist demonstrated the possibility of removing the phosphorus from molten pig iron by carrying out the conversion in a Bessemer vessel lined with a basic material instead of with a silicious lining, and by the addition of appropriate quantities of lime to the charge of molten iron. In 1879 the Thomas and Gilchrist process was tried on a large scale at Messrs. Bolckow, Vaughan and Company's Eston works. In the first blow they succeeded in reducing the phosphorus from 1.52 per cent. in the pig iron to .18 per cent. in the finished steel. As this was the first basic slag made on a commercial scale, a copy of the record showing the chemical history of the changes occurring may be of interest.

The record reads:—

May 3rd, 1879.

Metal Samples	Si	Graphite	Comb. Car.	Phos.	Time. Mn. Sec.	SiO_2	CaO	MgO	P_2O_5	Fe
Pig Iron	2.89	3.36	.06	1.52	—	—	—	Unusually high.	—	—
1.	2.21	2.64	.80	1.51	3-0	—	—		—	—
2.	1.43	.06	2.55	1.51	6-0	—	—		—	—
3.	.78	Trace	2.50	—	9-0	—	—		—	—
4.		Bad	Sample.							
5.	.13	Nil	.53	1.36	12-0	34.07	43.53	9.64	.60	5.00
6.	.10	,,	Nil	1.01	15-0	30.40	41.18	9.00	5.02	6.10
7.	Trace	,,	,,	.77	17-30	29.73	36.58	8.16	5.18	15.90
8.	Nil	,,	,,	.41	18-30	23.73	33.15	9.30	11.10	10.70
9.	,,	,,	,,	.12	19-30	20.93	35.62	8.50	10.94	13.50
10.	,,	,,	,,	.10	20-30		Bad	Sample.		
Steel ...	,,	,,	,,	.18 Mn..15	21-10	21.10	32.84	9.95	10.78	13.60

The phosphide of iron, Fe_3P, in which state of combination phosphorus exists in molten iron, is oxidised by reactions of the type.

$$5\ Fe_3O_4 + 2\ P = 15\ FeO + P_2O_5$$

$$5\ Fe_3O_4 + 8\ P = 15\ Fe + 4\ P_2O_5$$

The P_2O_5 formed may combine with FeO to form $Fe_3(PO_4)_2$ which, however, is unstable in the presence of a large excess of iron, and a reaction such as $3\ Fe_3(PO_4)_2 + 11\ Fe = 8\ FeO + 3\ Fe_3P$

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results, and it is in consequence of this reaction that the acid process of steel making is unable to remove phosphorus. In the basic process the presence of lime affords an opportunity to the phosphoric acid to form a stable body by the reaction

$$Fe_3(PO_4)_2 + 4\ CaO = Ca_4P_2O_9 + 3\ FeO.$$

The calcium phosphate formed is only feebly attacked and decomposed by the metallic iron, but manganese and carbon attack it more vigorously, and cause the phosphoric acid to be reduced and the metal to be rephosphorised. These reactions are, of course, proceeding concurrently, and it is necessary to maintain a certain concentration of ferrous oxide in the slag to minimise, as far as possible, the tendency to rephosphorisation. Rephosphorisation is probably due to the reaction between ferrous phosphate and lime being slightly reversible, whereby a small concentration of ferrous phosphate is always present, which is reduced by the carbon unless a source of oxygen is supplied by ferrous oxide in the slag.

At the termination of the blow, when the smelter has, by a test on the steel, determined that the phosphorus is reduced to the required limits, the convertor is gently tipped forward and the slag allowed to flow over the lip of the vessel into the slag pot, where it is allowed to cool or tipped molten, according to the arrangements of each particular works.

The Basic Bessemer process suffers from certain disadvantages which have caused it to be replaced to a great extent by the Basic Open Hearth process in one or other of its various forms. Essentially the difference between the processes lies in the source of the oxygen used for purifying the pig iron from its associated metalloids. In the Bessemer process the oxygen comes entirely from the air blast and the heat generated by the combustion of the silicon, carbon and phosphorus is sufficient to raise the temperature of the steel to a degree which is high enough to enable the steel to be cast into moulds. In the Open Hearth pig and ore process, however, which is the most important for the purpose of this discussion, the oxygen for purification of the pig iron is supplied, to the extent of about 70 per cent., by the action of the metalloids on oxide of iron, the reduced iron entering the bath of metal. The balance of the oxygen comes from the oxidising gases of the furnace. The operation is to charge iron ore and lime on a basic hearth heated by producer gas and to pour the molten metal over the heated lime and ore. The order in which the metalloids are oxidised in the Open Hearth process differs from that of the Basic Bessemer in a manner which has an important influence on the quality of the slag produced. In the Basic Bessemer process the phosphorus is oxidised and enters the slag at the end of the process, being the last of the metalloids to be removed from the iron into the slag, the richness of the latter in phosphoric acid depends on the original quantity of phosphorus in the iron, since the volume of slag made for a given pig iron is practically always the same. Even where very silicious iron is blown a preliminary slag, without lime additions, is formed and removed to bring the silicon under 1 per cent.

In the Open Hearth process the silicon and phosphorus are removed together, and if high grade slag is required the process is interrupted

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when the phosphorus in the metallic bath has reached about .2 per cent. and the charge tapped into a ladle provided with a spout over which the slag flows into another ladle or slag pot, the metal is returned to the furnace and the finishing heat completed. If the plant is equipped with tilting furnaces the slag may be removed by slightly tilting the furnace and pouring off the slag. Owing to the high viscosity of the slag, however, the separation of metal from slag is difficult, and to assist it a blast of air has been used in one German works to urge the slag towards the tap-hole and effect a more perfect separation.

In ordinary practice the Open Hearth process is not carried out as above indicated but by allowing the slag formed by the oxidation of the silicon, phosphorus and manganese to flow over shutes made in the fore-plates into slag-pots under the furances, and no attempt is usually made to remove more slag than that which flows out naturally when the level of the slag in the furnace is higher than the level of the fore-plate. The slag left behind is carried on and forms part of the finishing slag, which latter is therefore much greater in volume, and therefore lower in phosphoric acid than the slag removed in the middle of the process. By this method of operation the time spent in tapping the furnace for separation of the slag and for the formation of a new slag is saved, but the slag is inferior both in richness and in citrate solubility if that still forms a criterion of excellence to the agriculturist.

Tables II and III indicate the changes in composition of the slag by the two methods of operation.

TABLE II.

Y 508.—Making High Grade Slag.

No.	Time.	METALS.		SLAGS.					
		Car.	Phos.	Silica.	Lime.	Iron.	Total P_2O_5.	Sol. P_2O_5.	Cit. Sol. %
Molten Pig Iron			1.5						
1.	p.m. 2-20	2.16	.30	18.8	37.3	7.8	18.54	14.33	77.39
2.	2-50	2.11	.255	18.7	39.7	6.4	19.20	16.40	85.10
3.	3-20	2.08	.285	18.5	41.8	5.8	19.72	16.02	81.25
4.	3-50	1.88	.240	15.9	41.60	5.2	19.84	16.91	85.23
		Slag	removed and		new slag formed.				
5.	7-0	.70	·081	12.0	47.3	13.2	12.0	4.6	38.14
6.	8-15	.09	.018	9.4	51.3	14.6	7.4	11.10	14.9
				Steel	tapped.				

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TABLE III.

Z 603.—Ordinary B.O.H. Process.

No.	Time.	METALS.		SLAGS.					
		Car.	Phos.	Silica.	Lime.	Total Iron.	P_2O_5.	Sol. P_2O_5.	Cit. Sol. %
1.	p.m. 2-25	1.77	.300	20.30	33.2	8.60	17.08	15.36	89.92
2.	2-40	1.68	.327	19.90	34.8	7.30	16.87	14.85	87.89
3.	2-55	1.60	.35	18.80	35.70	8.40	17.30	15.49	89.53
4.	3-10	1.57	.335	20.30	34.90	6.20	17.08	14.08	82.43
5.	3-40	1.48	.321	20.20	37.00	5.60	15.85	11.90	75.70
6.	4-45	1.10	.19	20.50	37.70	5.50	15.66	11.78	75.22
7.	6-0	.74	.083	15.50	42.50	7.20	15.47	5.38	34.77
8.	7-0	.63	.07	15.10	40.50	7.00	15.75	4.99	31.68
9.	8-0	.14	.026	12.60	41.80	11.50	13.65	1.79	13.10
10.	9-0	.09	.023	10.20	47.80	14.70	10.85	1.66	15.30

The decrease in P_2O_5 content becomes quite sharp after the fourth sample, and this, it will be observed, coincides with the commencement of the period at which carbon elimination becomes predominant. If high grade slag is desired, it is removed at this stage, and after charging fresh lime and oxide of iron, the carbon elimination is proceeded with. It will be noticed that the phosphorus in the first metal sample is as low as in any of the four immediately following, and it may be asked why the slag could not equally well be removed at this stage instead of an hour later. The reason is that although the phosphorus is eliminated very rapidly (sometimes it is reduced to .3 per cent. twenty minutes after charging), yet it is necessary to delay the removal of the slag until all frothing has ceased and until the whole of the lime and ore are dissolved in the bath and the heat is sufficiently high to allow the slag formed to flow freely through the tap hole. Unless the slag is removed when it has reached the maximum concentration of phosphoric acid, the further additions of lime and ore and the denudation of the furnace structure under heat, cause an increase in the slag volume which reduces the phosphoric acid content until at the termination of the process it will contain from 7 to 10 per cent. only. As the content of lime increases, the slag thickens and reaches a viscosity which slows the progress of the "boil." This may be corrected by the addition of oxide of iron in the form of scale, but if sulphur has to be eliminated from the metal it is essential to keep the slag as basic as possible; the slag is therefore thinned by the addition of fluorspar, and it is this addition more than any other condition which reduces the solubility of the phosphoric acid in 2 per cent. citric acid. In

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Table III 1 cwt. of fluorspar was added after the sixth sample was drawn, and the soluble phosphoric acid fell from 11.78 per cent. to 5.38 per cent. immediately afterwards. In the smelting of steel, ferrous oxide goes into solution in the molten bath, and this reacts with the metalloids, principally carbon towards the end of the heat, forming carbon monoxide, which escapes into the furnace but leaves the steel and the slag saturated with respect to this gas at the temperature prevailing in the furnace. It is the function of the steel smelter to maintain a condition of slag such that the oxide of iron is as low as possible and for a sufficient time to enable the metal and slag to approach equilibrium conditions with respect to the dissolved FeO.

This latter condition conflicts with the necessity, as mentioned previously, of maintaining a certain concentration of FeO in the slag, and therefore in the metal, to enable the former to retain the P_2O_5, and a compromise has to be struck which would prevent so thoroughly deoxidised a condition being arrived at in the furnace as can be achieved in the acid process where the complication of the presence of phosphoric acid in the slag does not arise; this condition is counteracted, however, by the higher temperatures at which the basic open-hearth process can be operated without getting a wild charge, and with the additional advantage due to high temperature and highly basic slag of producing a steel of very low sulphur content. The finishing additions of materials such as ferro-alloys and carbon for completing the deoxidation and for bringing the steel to such a composition as will give the mechanical properties required are therefore made in the ladle before the slag begins to flow, a method of operation equally common in acid open-hearth practice. The slag which follows the metal on tapping is saturated with gas, which, as the slag passes through the solidifying range, is evolved very briskly, frothing up so as to occupy twice its volume in the cold state. It can be well understood that slag at a temperature of 1,500° C. in this lively condition is difficult to handle.

The ladle into which the charge of steel and slag is tapped is only sufficiently large to hold the steel, consequently the slag, being of lower specific gravity, remains on the top of the steel, and when the ladle is full overflows into a specially constructed slag ladle which is placed under the spout of the ladle (Fig. 2). A small stream of water is kept flowing into the slag ladle in order that the steam generated may help to disengage the gases evolved by the slag as it cools. The slag ladle is now run out of the melting shop on to a prepared tip, up the centre of which an inclined plane embankment is built, the mechanism of the tipping ladle is released, and the ladle, on tipping, projects the molten contents over the embankment, where, after being allowed to become solid, the slag is broken up into pieces capable of being loaded on to trucks by a grab. On removal to the grinding works the slag is passed through a rock crusher, which reduces it to about 2 in. pieces, it is then elevated into a hopper, from which it is fed to a ball mill, where it is reduced to about 10 mesh, and falls over a magnetic separator, to remove metallic shot entangled in the slag during cooling, into a hopper from which it is fed by a screw to the tube mill for final grinding to a fineness of 80 per cent. through a 100 mesh sieve.

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The tube mill consists of a steel cylinder slightly inclined from the horizontal towards the discharge end, it is lined with flint blocks wedged tightly into the sides of the cylinder, which is charged with 2 in. hard steel balls. The cylinder is direct coupled to a motor by a toothed steel band encircling it and causing it to rotate on its horizontal axis. The speed of rotation of the mill has an important bearing on its efficiency. A ball mill, which is simply a short steel cylinder lined with hard steel plates and charged with balls of 5 in. to 7 in. diameter, operates by the abrasion of the balls rolling over the plates and trapping the slag between their surfaces, for this purpose a slow speed only is necessary.

In the tube mill the speed is just sufficiently great to raise the balls to the highest point in the cylinder and cause them to cascade down to the bottom, the slag being caught between the falling ball and the flint lining. If the speed is too low the abrading action of the ball mill results, which for fine grinding is less efficient than the impacting cascade; if too high in speed the balls are carried past the highest point, and slide down the lining in the direction of rotation, doing very little useful work.

At the end of the tube mill is a receiving hopper, to which is attached an automatic bagging and weighing device. Samples are drawn from each bag and analysis done on the combined samples for the shift, a further sample is drawn and analysed for each order as it is loaded for despatch. Fig. 1 illustrates the tube mill, bagging and weighing device, and on the left an air bag filter for the removal of dust from the atmosphere.

In some plants the grinding is finished in a ball mill coupled to an air separator. The latter consists of two inverted cones, one bolted inside the other, so as to leave an annular space between them. At the top of the apparatus, (*i.e.* the base of the cone), a centrally mounted vertical power driven shaft carries fan blades fitted with a spreading disc. The slag from the ball mill is fed on to the disc, which, in rotating, casts it off into the current of air created by the fan blades. The fine material is carried over into the annular space and the coarse falls down inside the inner cone, each casing communicates separately by branches which enable them to be emptied, the coarse material being returned to the mill. The fineness can be controlled by regulating the speed of the fan or by adjusting a damper between the inner cone and the annular space.

A consideration of the figures in Tables II and III will explain how desirable it is for the farmer to determine the quality of the basic slag he prefers, whether high or low grade, and whether any solubility test is of value to him. The slag from the pig and ore process here described gives a valuable credit to the cost of manufacture, but it should be understood that this credit is merely a mitigation of the undesirableness of phosphorus in the ore and pig iron for steel making, and not a source of revenue to be sought for its own value. The Bessemer process, on the other hand, can use a high phosphorus pig iron with advantage, since not only is a richer slag recovered, but the heat of oxidation of the phosphorus is more than sufficient to provide heat for the fusion of the additional slag, while the time of oxidation is a negligible factor, as the reaction during the " after blow " when phosphorus is removed is at most a matter of minutes, whatever the phosphorus content of

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the pig iron. In the Open Hearth process a content of phosphorus in the pig iron exceeding 1.7 per cent. delays the refining considerably, especially if the slag is to be removed in fractions, as is necessary for the production of a rich and soluble by-product. The modern Open Hearth steel furnace, with all its equipment of cranes, charging machines, and hydraulically operated machinery, is too expensive an apparatus to use for the production or treatment of phosphatic manure, excepting when the removal of the phosphorus is necessary to the recovery of the iron in marketable form. Suggestions that mineral phosphates might be charged into the furnace for the enrichment of the basic slag would be practicable but quite uneconomical, as will be realised when it is remembered that the capacity of the furnace would thus be taken up by material of one-third the value of the steel and occupying three times the volume. If, however, a demand arises for a quality of slag which is not of the composition most suitable to the largest output of steel, it will be necessary for the farmer to offer inducements to the steel maker if he wishes him to furnish a slag which is high in phosphoric acid or possesses some quality making it especially valuable as a fertilizer.

The value of the slag as a by-product varies with the demand for steel; in times of high demand it is of greater commercial advantage for the steel maker to adopt a method of manufacture which will increase output even if the by-products and considerations of yield suffer, while in years of trade depression economy of manufacture is predominant, and the importance of yields and by-products is very great. It is in these latter circumstances that a high grade slag can be demanded at lesser cost to the farmer. Any concensus of opinion which may emerge from this discussion and which will indicate to the steel maker the direction and probable value of different grades of basic slag will certainly have the effect of causing the steel maker to bend his efforts to the production of slag having the desired qualities.

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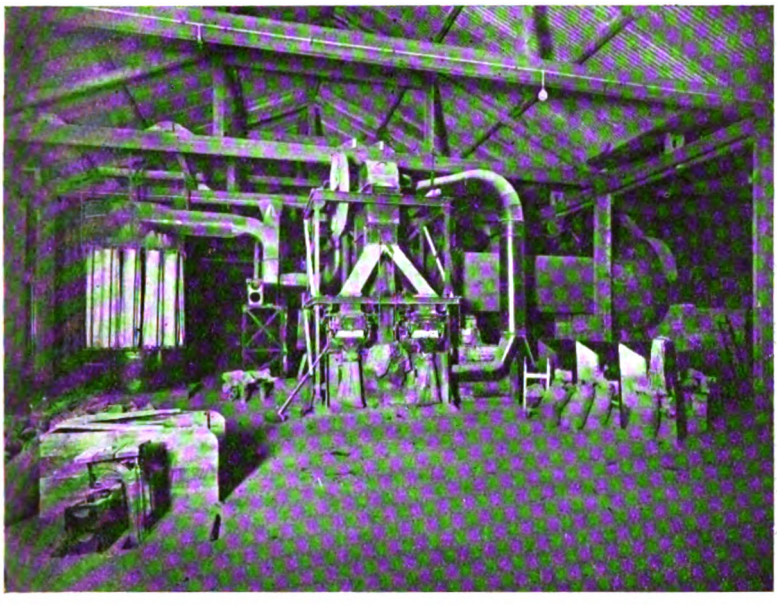

FIG. 1.
Tube Mill, with Automatic Filling and Weighing Machine.

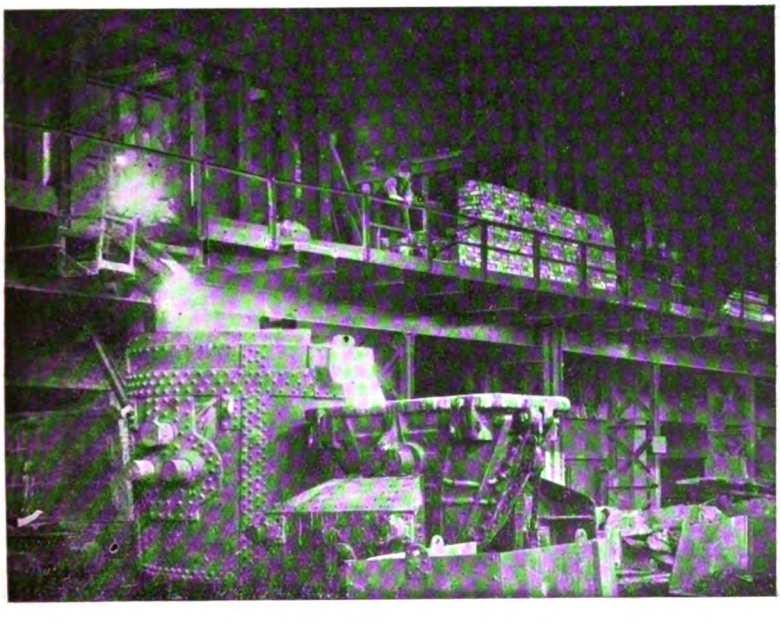

FIG. 2.
Basic Open Hearth Furnace: Basic Slag overflowing from Steel Ladle to Slag Ladle.

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Mr. W. S. Jones read a paper on "The Improvement of Low Grade Basic Slag."

THE IMPROVEMENT OF LOW GRADE BASIC SLAG.

By W. S. Jones, M.A., M.Sc.

The problem which surpasses all others in importance in relation to basic slag is the prevention of waste, more especially by the improvement of the grade. The various ways I propose mentioning for improving the quality may be conveniently classified as follows:—

(1) Concentration methods by mechanical means; (2) manipulative methods; (3) direct enrichment methods by using phosphate rock, and (4) process methods.

(1) *Concentration Methods by Mechanical Means.*

The methods falling under this heading are perhaps more of academic interest than of any great practical value. Two methods may be cursorily noted:—

Firstly—*The utilisation of differences of specific gravities in the constituents to separate the inert and worthless matter from what are usually regarded as valuable and essential constituents.*

This was tried on a small scale during the war. Some measure of success was met with, but a maximum increase in the phosphate content of about 12.45 per cent. was insufficient to justify the method employed. The original slag was washed on a concentrating table, and the necessity of subsequently drying the slag rendered the method impracticable. A dry method, involving a process of winnowing, might be tried, but I doubt whether adequate success would be attained.

Secondly—*The utilisation of differences in the grindability of the slag constituents.*

It is conceivable that the phosphates in slag are more easily pulverised than some of the other ingredients, such as iron compounds, and that they attain a sufficient degree of fineness before some of the more inert constituents do. If so, it is possible that by a system of sieves in the grinding plant it could be arranged for a good deal of the phosphates in the low grade slags to be separated from the more refractory constituents.

(2) *Manipulative Methods.*

When the constructional arrangements of the steel furnace make it possible to secure a double tapping of the slag, the poorer material can be discarded. This must not be considered necessarily as a loss of slag, for it is presumed that we are considering slags of low quality

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and probably worthless without the adoption of selective tapping or some other means of improvement. The matter, of course, largely resolves itself into one of expense. In the case of furnaces where only a final tapping is secured, a process of selection is to some extent now practiced, and the slag is separated into:—(1) Ball slag, and (2) pie slag, the latter containing a larger admixture of steel.

(3) *Direct Enrichment Methods by Using Phosphate Rock.*

It has been suggested that finely ground, high grade phosphate rock might be added to the molten slag during the process of tapping. I have grave doubts as to the advantage of this method. Theoretical considerations rather indicate that this process would not increase the solubility of the added phosphate, and while I do not know the measure of success obtained in some recent experiments, my information is that earlier experience confirmed the view that no advantage would accrue.

Take, again, the plan of adding phosphate rock to the open hearth furnace charge. This, while it would improve the phosphatic content of the slag, would have too many and too formidable drawbacks. Moreover, experiments so far carried out do not appear to have yielded satisfactory evidence that the solubility of the phosphate is increased unless the charge be allowed to remain too long in the furnace.

It seems safe to assume that the use at steel works of phosphate rock for the purpose of improving slag can only be justified if the solubility of the phosphate rock is to some extent increased by subjecting it to the conditions existing in the steel furnace or by mixing it with the hot slag during the process of tapping. Unless some change be effected in the state of the added rock, there can be no reason for its addition to the furnace or hot slag, for an equal improvement could doubtless be secured by the much simpler method of mixing the phosphate rock intimately with the cold slag before grinding.

(4) *Process Methods.*

These are probably the most important and most generally effective.

Perhaps one may, in order to make matters clearer, be forgiven for reviewing very shortly the operations to which iron ores are subjected in their conversion to steel. One of the first main processes which iron ore undergoes is treatment in the blast furnace. The purpose of this process is to separate the iron of the ore from the gangue with which it is associated. The bulk of the impurities are removed in the blast furnace slag which is formed, but some carbon, silicon, and sulphur derived from the ore and practically all the phosphorus in the ore combine with the iron, which gradually descends to the hearth of the furnace where it is tapped.

The conversion of pig iron into steel is the next step, and this consists essentially of the removal to the required degree of the carbon, sulphur, silicon, and phosphorus which are present in the pig iron. In the case of basic pig iron this is done either in Bessemer converters or open hearth furnaces with a basic lining. The charge consists of

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pig iron, lime, and varying quantities of scrap metal. The impurities of the iron, including the phosphorus, pass into the slag which is formed.

One cardinal difference between the Bessemer and open hearth processes is that phosphorus constitutes an important source of heat in the former, while in the latter it has no such significance. For the Bessemer process a high phosphorus content is a decided advantage; for the open hearth process the more phosphorus-free the pig iron is the better.

After that meagre description of the processes of steel manufacture, one may mention two or three ways by which an improvement in the basic slag could be effected. One means is:—

By a Reduction in the Amount of Scrap used.

A reduction in the amount of scrap used in the steel furnace charge would improve the quality, but the use of scrap is controlled by:—

(1) The relative cost of pig iron and scrap, and

(2) The amount of scrap available.

The abundance of scrap is again governed largely by the type of mills at the steel works. No one could, of course, expect steel makers to waste metal in order to produce slag.

A very successful way of improving slag is:—

By the Addition of low-grade Basic Slag or high-grade Phosphate Rocks to the Blast Furnace Charge.

When the steel plant consists of Bessemer converters, the blast furnace is often made use of for the purpose of enriching slag. Low-grade slag is frequently returned to the blast furnace with a view to salving the phosphorus which would otherwise be lost. The phosphorus passes over into the pig iron with the phosphorus originally present in the ore, and ultimately reappears in the form of enriched slag. The low-grade slag may be replaced by phosphate rock, and in this way some of the richest slags are obtained.

So in the case of the basic Bessemer process, where a high phosphorus content is useful, the improvement of slag is a perfectly simple operation. But how is one to effect slag improvement, so often necessary in the case of the open hearth process, where a pig iron as free from phosphorus as possible is considered so desirable? In the presence of practical men I would suggest with much hesitancy in this connection the adoption, if possible, of:—

The Principle of the Bertrand-Thiel Process.

In this process, which is a modification of the open hearth process, two furnaces are used in the place of one. In the primary furnace pig iron without scrap is worked with a highly basic slag. Simultaneously scrap, oxide of iron, and limestone are heated to a high temperature in the secondary furnace. When practically all the silicon and phosphorus have been removed in the primary furnace the metal is transferred from the primary to the secondary furnace, where the process is completed. As no scrap is used in the primary furnace, the slag is not diluted thereby, and a grade containing a

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high percentage of silicon and phosphorus can in this way be obtained. The bulk of the phosphorus having been eliminated in the primary furnace, the slag from the secondary furnace is necessarily low in phosphoric acid.

This system has not found favourable acceptance in Great Britain. Nevertheless, the question obtrudes itself whether the principle of the process, as distinct from the process itself, cannot be adopted to conditions prevailing in this country.

The Bessemer process of steel production seems gradually to be passing, to be replaced by the open hearth process, but there appears to be a good deal of reason for retaining the basic Bessemer converter, not as a steel production plant in the ordinary sense, but for the avowed purpose of basic slag production at iron works.

The Bessemer converter would in this case play an analogous part to the primary furnace of the Bertrand-Thiel process in removing the phosphorus. This would mean the introduction of an additional process at the iron works, but it is likely that the installation of converters could be carried out at a minimum of cost. The adoption of this plan would have very great advantages from the point of view of slag production, and it does not appear to me that it would in any way complicate or render more difficult the operations subsequently to be carried out at the steel works. Indeed, this preliminary removal of the phosphorus might even facilitate the subsequent treatment of the metal in its conversion into steel in open hearth furnaces, and might enable steel makers to employ in certain cases acid furnaces even for iron derived from phosphoric ores. The problem, therefore, resolves itself entirely into a question of cost and adaptation of processes. If the assumption just made prove correct, some relief should be got from the greater value to the steel makers of the dephosphorised iron.

It has been mentioned that in using the basic Bessemer converter the presence of a high percentage of phosphorus in the pig iron is highly desirable. So with the introduction of the extra step proposed, whenever there was any doubt as to the quality of the slag from a particular ore being sufficiently good, high grade phosphate rock could without detriment be introduced into the blast furnace charge with a view to strengthening the phosphorus content of the pig iron. In this way slag of any quality could be obtained at will, and the enormous waste of phosphates now taking place would forthwith be reduced to a minimum. Moreover, the adoption of the step indicated would afford a means of recovering a large proportion of the enormous dumps which have up to now been regarded as waste heaps.

In conclusion, I should like to say just a word relative to the mixing of phosphate rock and low-grade slag with a view to improving the grade of slag. While it is common practice to talk of the improvement of basic slag by increasing its phosphate content by the direct addition of phosphate rock, I sometimes wonder whether it is likely that the non-phosphatic constituents of slag exercise an ameliorating influence on the soil. If so, it might be possible to use with advantage even the lowest grades of basic slag by their employment to make good possible defects in the non-phosphatic constituents of high-grade rock.

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General Discussion.

The Chairman: I think we have listened to a very interesting paper by Mr. Jones, and he has certainly asked the steel makers some questions which it will be very interesting to have answered. We have a paper by Dr. Desch (p. 272), but he wants to modify it somewhat before it is published, and there is also a paper by Sir Daniel Hall (p. 283) which I propose to read briefly after the discussion, if there is time. He emphasises the point which has already been made by Sir T. Middleton and Dr. Russell, viz., the enormous importance of basic slag to this country in increasing the production from grass land. He deals largely with questions about which we have already heard a good deal. The situation now resolves itself into this; we have heard from the agricultural standpoint the necessity for a large supply of basic slag of the right sort, and the question is, how can the steel makers give the supply that is required. Dr. Stead has already spoken from the steel makers' point of view, and I will now ask Mr. Hutchinson, of the Skinningrove Iron and Steel Works, to speak.

Mr. A. Hutchinson: I should like to congratulate the Faraday Society on the very interesting discussion and the large number of papers which we have heard to-night. It has been said that we are not to allow the tail to wag the dog, and that is quite right, but on the other hand I want to say that we are not therefore going to dock the tail off the dog. We are all very alive in the steel trade to the great importance of this basic slag question, and we want to do everything we can to supply the country with the slag it wants, but we are faced with this position at the present time that, as has been stated, the basic Bessemer process is going out. At any rate, it has practically gone in our district, and it was the conditions in the process which gave the slag which was required.

In the basic open hearth process, as has been pointed out, the conditions are not advantageous to the production of high grade slag, but the present position is that there is a very considerable improvement, and I should like the basic slag users to know that. Until a few years ago we had heaps of slag which it was very difficult to get the merchants or the grinders to take, but now practically all we are making up to 14 per cent.—I do not think we get it much higher—is going into regular use, and that is being mixed. We do not ask the grinders what they mix it with, but it is probably mixed with the higher grade slags and some of these other minerals which have been suggested to-night. But the satisfactory part of it is that it is all being used, and therefore there is not the waste which was going on in the early years with the basic open hearth process. That is all to the good, and I think the very fact of these papers having been read and that the chemists are reading these papers, shows that during the last two or three years, at any rate, we have been paying very great attention to this, and we hope to be able to increase the proportion of basic slag. It is quite true that we exist to make steel, and that has also been

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said of allied processes, that the coke ovens, for instance, exist for making coke, but we have long since learned that other by-products can also be obtained, and these are of great national importance. We are giving attention to this in the steel industry, and you can rely on it that our research chemists are doing all they can to help you in that way. There are not only basic slag manures, because some of our chemists are working in other directions, and I hope within the next week we shall be making large quantities of potash manures.

Mr. E. H. Saniter: The question of basic slag is one with which I have been connected now since 1883, when I was at a Bessemer works where they made this very rich slag about which we have heard so much to-night. I may say, however, that in the future you may look upon basic Bessemer slag as a thing of the past so far as manufacture in this country is concerned. I believe, although I am not quite sure, there is not one basic Bessemer plant, and there is certainly not more than one, and therefore for all practical purposes if you want basic slag you have got to have open hearth slag. We have heard a good deal about it to-night, and I do not think I need say anything more on the subject.

On the question of the citric acid test in relation to the two classes of slag, it has been pointed out by Mr. Robertson that by using one gramme, a very much greater solubility is obtained, as compared with using five grammes, assuming you use the same volume of 2 per cent. citric acid. When you consider that the 18 or 20 per cent. phosphoric acid slag contains much less free lime than the lower grade slag, you naturally would assume that the lime would have a less neutralising effect on the 2 per cent. citric acid, and that therefore you would get greater solubility. Dr. Russell has referred to the question of the free lime in the slag as being a valuable constituent, and he refers to 4 or 5 per cent. of free lime. That may be quite correct with reference to the high phosphoric slags, but as a matter of fact, with these low phosphoric slags, where there is a large excess of lime, practically the whole of the lime uncombined with fluorine and the phosphorus is soluble in water if sufficient time is given, and even that combined with silica is soluble in water, so that there is a very large percentage of available and valuable lime in the low grade phosphoric slags with fluorspar in them.

Sir T. H. Middleton referred to the question of the bullocks per acre, and it naturally occurred to me to consider the question of the ton of basic steel and the proportionate amount of basic slag per acre of arable land in this country. I believe that the make of basic steel is, according to the last figures we have, between four and five million tons in the whole of the country, but if we take it at five million tons, and that one quarter of that is the equivalent weight of slag produced, we therefore have only $1\frac{1}{3}$ cwt. of basic slag produced in the country per acre, and I am afraid that would not make all the difference in beef that Sir T. H. Middleton talked about, if it were all on the arable land.

Mr. Jones and others have referred to the question of endeavouring to enrich the slags. The selective tapping of the slag to

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obtain a rich slag is to a certain extent possible, and is practised in connection with the molten metal open hearth processes. It is impracticable, however, when working with cold pig and scrap, and I doubt whether the advantage gained—I am speaking from the steel maker's point of view—even in the partial tapping, compensates for the extra cost of proceeding in this way. With regard to the question of putting mineral phosphates or anything of that sort into the slag, either in the ladle or furnace or in the slag ladles afterwards, I am in entire agreement with previous speakers that it is impracticable, and it seems to me that if you wish to enrich the slag the only way, as suggested by Dr. Stead, is to grind the mineral phosphate and the slag up together as a final process, if there is any advantage in doing so. With regard to the suggestion of Mr. Jones for improving slags by running the Bessemer process as a by-product process, I do not know what he is going to do with the steel. We none of us thought much of it when we had it. I do not think there would be any possibility of working in that way economically, and as for making steel in a Bessemer converter with basic lining to get phosphorus out, and then putting that steel into the basic open hearth, that would be absolutely uneconomical, owing to the enormous waste of valuable metal which would take place.

Mr. C. H. Ridsdale: I am very much obliged to you for inviting me to your most interesting meeting, because I have been connected with basic slag manufacture in its various stages from the very beginning. I may first say, from the manufacturing point of view, that it is perfectly right that sand and phosphate are not properly miscible. We tried everything in that way that we could think of, but there were such little things as the sand being damp. If you tried to put in damp sand, and it always is damp, into the molten slag running into the ladle, it does not give a good effect. Then there is always wind about in the steel works, and if you try to put powdered phosphates in, these valuable bodies blow away. Then, again, phosphates always seem to be based upon the price of slag, and therefore you never can get the phosphates cheaply enough to add them in the blast furnace or the ladle. There was a time when we could not get a good enough iron for practical purposes, *i.e.*, when we could only get 1.5 per cent. phosphorus instead of 1.8 per cent., and then it paid to add a little Belgian phosphate in the blast furnace, but that was mainly to help the steel making.

Leaving manufacture, I come to these crystals, which I thought would be of interest as being the original crystals from which we were able to isolate the constituents of the slag; these are some 34 years old. I will not say anything more about them than to refer you to three papers which anybody who is interested can look up. There is one given to the Chemical Society in July, 1887, by Dr. Stead and myself; one to the Iron and Steel Institute in May, 1887, which was a little bit more practical than the one to the Chemical Society, but does not deal so much with the crystallography; and then there is one which is a good deal more practical and deals with this question of solubility and excess of lime rendering it insoluble, to the Cleveland Institution of Engineers, on "The

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Solubility of Basic Slag." That was in January, 1895, and was by myself. I will not say more, because these references will enable anybody to follow the matter up who wants to, but I think we can take it that if you sum up the whole of the evidence broadly, as regards the ordinary kinds of slag, apart, perhaps, from fluor-spar slags, the more soluble basic Bessemer and the less soluble basic open hearth, one is practically as good as the other per unit of phosphoric acid. You may have to wait a little bit longer for your return when you put an insoluble phosphate into the ground, but you will get it. It is a question of speed. If you grind it sufficiently finely you will get speed.

Dr. Russell said that probably there was some constituent besides phosphate of lime which accounted for the remarkable benefit got from basic slag. I am not an agriculturist, but I have a very strong feeling that there it is due largely to one which he did not mention, and that is iron. In basic Bessemer slag you have got, as you will see from these crystals, three distinct compounds of lime and iron in which oxides of iron act as the acid and lime as the base, and the result is that they are very easily decomposible. Atmospheric influences, with water, carbonic and humic acids, will decompose them, and therefore you get a soluble iron, and there is no question that a soluble iron does facilitate the formation of chlorophyll, and on the chlorophyll—just as the red blood corpuscles of human beings is essential to their life—depends the life of plants. There is a striking example of that. Round about the North Yorkshire moors there are a lot of calcined shale heaps which are quite a bright red colour in places, and all along these heaps you have brilliant green grass growing freely. There had been strong emphasis laid on the question of our need for phosphates. If the steel makers cannot make enough phosphates, there is another source in our own country.

Quite recently, within the last year or so, it has been brought to my notice that there are some deposits of iron ore that are quite as high in phosphoric acid as the average basic open hearth slag. In the raw state there is about 25 per cent. iron, and 9.5 phosphoric acid, working out at nearly 21 per cent. of phosphate of lime. If it was worth while, that could be calcined and would yield from 25 to 27 per cent. of phosphate of lime, *i.e.*, tri-basic phosphate, but I do not think it will pay to do this, as there is no object in calcining it to get a richer material except possibly to reduce the cost of transport. For the past year I have been trying some careful experiments with that ferruginous phosphate which is simply a poor type of ore containing phosphate pebbles, and some of it has been ground to the fineness of basic slag. I have tried it systematically upon definite garden plots against various other manures, and I got the most remarkable results, not with corn, however, which I did not try. I tried peas, broad beans, ordinary greens of the cabbage type, potatoes, roses, and sweet peas. These latter I tried with a view to reducing disease by strengthening the stems, because I understood that iron was good for that, and there is no question that we got very remarkable results. We were eating green peas in October, and we had the finest potato yield I have ever seen. We had roses very late in the year, and free from disease, when in the

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previous year they had been mildewed. Of course, that is only just one year's experiments, and I believe that Mr. Robertson has been trying some experiments with the same substance, and he can also tell you that he got most remarkable results. I think it was grass in his case; so that here you have two substances, iron and phosphoric acid, which are very soluble—I am not speaking in the ordinary citric solubility sense—but to ordinary carbonic acid and atmospheric influences, humus acid, and so on, and which simply needs grinding and putting on the land. Therefore I have no doubt that these also will come in and help out the slag towards supplying our great national need.

Dr. R. E. Slade: I should like to ask some of the steel makers if they will be kind enough to explain why calcium fluoride is used in the open hearth basic process to remove sulphur, and also what proportion of the cost of the basic slag on the market is represented by grinding.

Mr. D. Sillars: The cost of grinding is about 30s. per ton of slag.

There is another word I should like to say in discussion of Mr. Jones' valuable paper. The process which I mentioned in my previous remarks is exactly the same as the Bertrand Thiel process, except that it is carried out in one furnace instead of two. The two furnaces were not found practicable because they could not be precisely timed to one another, and delays affecting output resulted. The process was originated at Hoesch, and it is sometimes known as the " Hoesch " process. The principle of adding phosphates to the blast furnace to produce an iron rich in phosphorus and consequently a rich slag is quite unsound if the basic open hearth process of steel making is to be used. The phosphoric acid so added must be reduced to enable it to combine with iron as iron phosphide, this reduction absorbs a considerable quantity of heat at the hearth of the blast furnace, the cost of which forms a distinct item in the balance-sheet of the furnace. Having so reduced the phosphoric acid, we promptly proceed to liberate this heat under disadvantageous conditions which enable us to recover only a small proportion of it as useful energy. So long as phosphates can be obtained as mineral phosphates, it is essential that these points should not be overlooked, as they involve the very urgent question of fuel economy. With this in mind I think the case for enriching slag in the manner suggested falls to the ground unless the phosphorus is a source of heat as in the Basic Bessemer process now falling into disuse.

Sir Thomas Middleton: One speaker has drawn attention to the fact that even with 1¼ cwt. of basic slag available per acre one could not get a great increase in beef production. But his figure was 1¼ cwt. per acre per annum, and this amount per annum means in nine years some 11 cwt. of manure. An untreated plot on Tree Field at Cockle Park, Northumberland, produced 8½ cwt. hay on an average of a period of nine years. A plot which received at the beginning of the nine years, 1897-1905, 10 cwt. of basic slag per

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acre produced three times as much hay and more than three times as much mutton over the whole period. One must not think that because one had only 1¼ cwt. per annum available that this is a negligible amount. It would be very valuable if accumulated and used as it ought to be at considerable intervals. It is the worst possible economy in improving poor land to put on basic slag small dressings. The object of applying basic slag is to get clover to grow before the grasses grow and come into competition with it, and the right method of applying basic slag is to apply in large quantities, say 8-12 cwt. per acre. It is only then that one gets the maximum results from its use on poor clay pastures.

Dr. E. J. Russell: With regard to the question of adding mineral phosphate in the slag and grinding afterwards, I do not think that would be acceptable from the agricultural point of view. I should like to say what a very great pleasure it is to see Mr. Ridsdale. We have heard of his name in connection with slag, but I have never yet had the pleasure of meeting him. A point I should like to refer to is that of the iron he mentioned. I know of few soils in which iron is deficient. One recognises that iron is an essential plant nutrient, and that in sand cultures or in extreme cases it might be valuable A good many attempts have been made to use iron compounds as fertilisers, but so far without success on normal soils, but I should be quite prepared to examine any that Mr. Ridsdale supposes to have exceptional qualities.

There is a practical agricultural proverb that you should make hay while the sun shines, and before sitting down I think that whilst we have steel makers and agriculturists here it would be a very good thing if we could arrange that there should be some outcome of this discussion apart from the mere printing of an account which might be filed or put on our bookshelves and forgotten. I should like to put out the suggestion that it would be well to set up a small sub-committee consisting of a few steel makers and a few agriculturists to see if it is not possible to carry on this subject to some practical outcome. I am quite sure the agriculturists would do all they possibly can to help, and I am perfectly certain that the steel makers like Mr. Hutchinson, Mr. Sillars and others whose names I need not mention, would do all they can to help. I think it would be a great pity now that the agriculturists and the steel makers have come together to discuss this question if nothing practical resulted, and I should therefore like to suggest that a small sub-committee should be constituted to carry this matter to a further stage and see what can be done.

Mr. C. H. Ridsdale: With regard to the iron question, perhaps I did not bring it out so clearly as I ought to have done, but it is a soluble form of iron. That is what I have tried to bring out in connection with these iron-lime compounds and this ferruginous phosphate. If you get a fused, vitreous, silicate of iron, or a silicate of iron and manganese combined with the phosphate of lime, then they are very insoluble, as these lemon coloured needles show. You cannot get such a thing as siliceous mill cinder to dissolve which is mainly silicate of iron. I think the suggestion about the Committee an excellent one.

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Mr. L. Weaver: As the official representative of the Ministry of Agriculture present to-night, I am sure the Ministry would welcome very strongly Dr. Russell's most admirable suggestion. It is my duty to discuss these matters with the grinders of basic slag from the point of view of agricultural supplies, and if the Ministry of Agriculture can help in any way to forward the deliberations of such a Committee, we shall be very glad to do so.

Mr. E. H. Saniter: The question was asked as to why fluorspar was used to remove sulphur in basic open hearth processes. If the gentleman who asked the question wants me to give him a chemical formula for that, I am afraid I cannot, but the practical matter about it is this, that the addition of fluorspar to the slag in the basic open hearth furnace allows you to use a slag of sufficient liquidity much richer in lime than can be used without the presence of fluorspar, and it is necessary in order to get successful desulphurisation to have from 50 to 53 per cent. of lime in the slag of the basic open hearth process, and by that means the richer lime slag, presumably, has a considerably stronger affinity for the sulphur than the iron has.

The Chairman: You get a greater liquidity with a higher lime content?

Mr. Saniter: Yes.

Dr. T. M. Lowry: With regard to grinding, a fineness of 100 mesh was mentioned, but for Portland cements grinding to 180 mesh fineness is used, and in the case of pigments the grinding is very much finer. If therefore basic slag is only ground to 100 mesh it should be possible to get it more finely ground, and in this way counterbalance the diminution of solubility caused by the addition of fluorspar.

Mr. D. Sillars: You can get any fineness you like. The present standard is 100 mesh; 76 per cent. on a 100 mesh, and you could get 3 per cent. with 180, according to whether you used a tube mill or a ball mill with separator.

Dr. E. J. Russell: We have no agricultural evidence that there is any advantage in going beyond 80 per cent. on a 100 mesh sieve, which is customary, but at the same time I am afraid that in any case the evidence is not particularly good, because it is based on general experience rather than precise experiment.

The Chairman: I wonder how we could best forward the most interesting and practical suggestion made by Dr. Russell with regard to the formation of this Committee.

Dr. E. J. Russell: I should suggest the Committee consist of three or four steel makers and three or four agriculturists, and possibly one representative of the Ministry of Agriculture--all men prepared to do something.

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Mr. A. Hutchinson: As the researches that have been going on have been under the auspices of the Carnegie Research Fund, from which grants have been made by the Iron and Steel Institute, I think it would be courteous to refer the matter to the Institute.

Mr. Laurence Weaver: It would also be an advantage if we could have representatives of firms who grind slag and sell it. They know the commercial side of the question, which would be useful.

May I add that I am quite certain Lord Lee would be willing to take any steps to invite the gentlemen suggested to form a Committee. We all know that the idea has been initiated here, but if there would be any advantage in it the Ministry would be only too pleased to call the Committee together.

Dr. Russell: I think that would be a very good plan. The suggestion will come from the Faraday Society in the first instance as the outcome of this Meeting; it will then go to the Ministry and they will communicate with the Iron and Steel Institute, and the Ministry will see, I hope, that the proper persons are appointed.

Mr. G. V. Parker (South Wales Basic Slag Co.): May I suggest that before the Committee asks the steel works to carry out experiments in enriching their slag, it would be advisable for the experiments in the field to be further continued. We should like to know what is the real value of basic slag. In all the experiments I have heard of they have always been based on phosphoric acid content, so many pounds of phosphoric acid to the acre. No account has been taken of other ingredients which might have a detrimental effect or otherwise. There should be more evidence as to the real action of basic slag in the field, and, speaking as a slag grinder, I think it is desirable for extensive experiments on the soil to be carried out first. I only throw that out as a suggestion.

The Chairman: I think that when the Committee comes together these are points which will be discussed, and that criticism will be taken note of.

The meeting concluded with the unanimous adoption of a resolution recommending the Ministry of Agriculture and Fisheries to create, in consultation with the Iron and Steel Institute, a permanent Committee to study the Basic Slag problem, consisting of three or four Steel Makers, three or or four Agriculturalists and Agricultural Chemists, a representative of the Fertiliser Trade, and a representative of the Ministry of Agriculture.

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ON THE VAPOUR-PRESSURES OF MIXTURES.

By Alfred W. Porter, D.Sc., F.R.S.

(*A Paper read before* The Faraday Society, *December* 15, 1919.)

PART I.—BINARY MIXTURES.

The fundamental equation concerning the vapour pressures of binary mixtures is undoubtedly the differential equation of Duhem, published in 1887* (Traité de Méchanique Chimique, t. iv., Chap. VII.).

This equation may be written

$$\mu_a \frac{\partial \log \pi_a}{\partial \mu_a} = \mu_b \frac{\partial \log \pi_b}{\partial \mu_b}$$

where μ_a and μ_b are the molar fractions of the components in the liquid mixture and π_a, π_b are the respective vapour pressures. This equation is nearly exact under ordinary conditions, though it assumes that the vapour mixture follows the law of perfect gases (in consequence of which the partial pressures of its components are additive), and further that the liquid volume is negligible compared with that of the vapours from it. These assumptions do not impair the utility of the formula excepting in those cases for which one or other, or both of the components, approach close to their critical points.

The proof of this important theorem as usually given is somewhat obscure. A diagram of the thermodynamic cycle which is employed is a great help. The following proof is given as an attempt to make the demonstration clearer:—

Let a volume V of a binary mixture at pressure, p, equal to the total vapour pressure be taken and let the vessel in which it is contained be provided with semipermeable membranes each permeable to one only of the two components (Fig. 1). These membranes communicate with

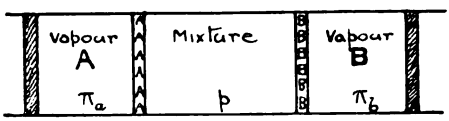

Fig. 1

* Subsequently, but independently, obtained by Max Margules. Sitzungsberichte K. Acad. d. Wien, *104*, 1243 (1895).

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lateral chambers provided also with impermeable pistons. The substance which passes into one of these chambers when the pistons are suitably moved will consist of one component alone; in the left-hand chamber vapour A alone, in the right-hand chamber vapour B alone. These lateral chambers will at first be of zero volume; that is, the impermeable pistons are to be in close contact with the semipermeable ones. It is convenient to represent the changes that will be made by means of two diagrams, one for vapour A, one for vapour B; or, in the proof of the exact formula, these together with a third diagram for the liquid mixture.

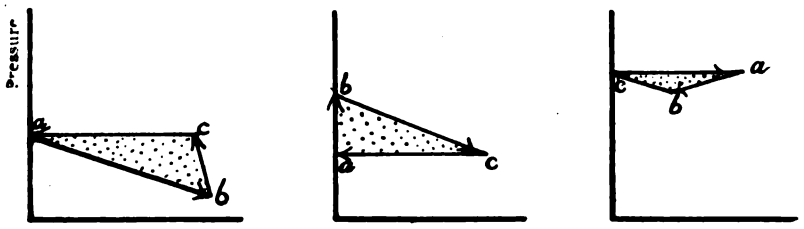

FIG. 2.

It will be premised that if any of A be removed from the mixture its vapour pressure will diminish, because its concentration diminishes, while simultaneously the vapour pressure of B increases because its relative concentration increases.

The following changes, which are to be made isothermally and reversibly, will complete a cycle on each of the three diagrams. The masses in the liquid mixture are M_a and M_b.

Change.	Path on diagram A.	Path on diagram B.
Transfer a mass fM_a of A where f is a small fraction to chamber A. The pressure in A chamber changes during the process by $-d\pi$ while that on the B piston increases by d_{π_b}	*ab*	*ab*
Separate the vapour in A chamber and compress it to original pressure π^a	*bc*	none
Transfer fM_b of B where f is the same small fraction to chamber B. The pressure in B chamber diminishes and the vapour pressure of A increases.	none	*bc*
The original concentration is now restored and the mixture is in equilibrium with the components. The vapour of A may now be brought again into communication with the mixture through its semipermeable membrane.		
Push both vapours back into mixture in such a manner as to keep the concentration constant throughout.	*ca*	*ca*

The algebraic sum of the areas of these isothermal cycles must be zero

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In the limit the area of the A cycle is $-\frac{1}{2}fM_a v_a \frac{\delta \pi_a}{\delta M_a} dM_a$ as can be seen by inspection; and that of the B cycle is $-\frac{1}{2}fM_b v_b \frac{\delta \pi_b}{\delta M_a} dM_a$

Hence

$$M_a v_a \frac{\delta \pi_a}{\delta M_a} + M_b v_b \frac{\delta \pi_b}{\delta M_a} = 0.$$

So far the changes in the mixture are neglected; they are represented in the mixture diagram, the area of which is $\frac{1}{2}f\left(M_a s_a + M_b s_b\right)\frac{\delta p}{\delta M_a}$, whence the exact expression is

$$M_a v_a \frac{\delta \pi_a}{\delta M_a} + M_b v_b \frac{\delta \pi_b}{\delta M_a} - \left(M_a s_a + M_b s_b\right)\frac{\delta p}{\delta M_a} = 0.$$

In the last two expressions s_a and s_b represent the shrinkages of the mixture when unit mass of either A or B is withdrawn the other being kept constant; *i.e.*

$$s_a = \left(\frac{\delta V}{\delta M_a}\right)_{M_b} \qquad s_b = \left(\frac{\delta V}{\delta M_b}\right)_{M_a}.$$

Since $p = \pi_a + \pi_b$ if we assume the vapours to be perfect gases, and s_a s_b are small compared with v_a v_b, we may usually neglect this term relating to the changes in the liquid mixture.

If v_a and v_b are made to mean *molecular* volumes (instead of specific volumes) the approximate expression can be written

$$\mu_a v_a \frac{d\pi_a}{d\mu_a} + \mu_b v_b \frac{d\pi_b}{d\mu_a} = 0,$$

where μ_a and μ_b are the molar fractions of A and B in the liquid mixture and the differential co-efficients are now total differential co-efficients.

Since $\mu_b = 1 - \mu_a$ and therefore $d\mu_b = -d\mu_a$ the equation may be written in the form given at the beginning of this paper if $\frac{RT}{\pi_a}$, $\frac{RT}{\pi_b}$ are inserted instead of v_a and v_b.

Duhem's equation is a differential one containing two dependent variables π_a π_b and is therefore indeterminate. It imposes one condition only which is equivalent to asserting that each side of the equation must be a symmetrical function of μ_a and μ_b. We may assume this function to be expanded in powers of the product $\mu_a \mu_b$. This may be possible because $\mu_a \mu_b$ is never greater than 0.25 and decreases to zero each way towards extreme values of μ_a and μ_b. The equation was integrated by Margules on these lines. If for simplicity we deal only with the first power and write

$$\mu_a \frac{d \log \pi_a}{d\mu_a} = a + \beta\mu_a(1 - \mu_a)$$

the integral for π_a becomes

$$\log \pi_a = \text{constant} + \log \mu_a + \beta - \beta\frac{\mu_a^2}{2}$$

which for the case $\pi_a = \Pi_a$ when μ_a is 1 becomes

$$\pi_a = \Pi_a \mu_a e^{\beta(1-\mu_a)^2}.$$

Similarly

$$\pi_b \Pi_b (1 - \mu_a) e^{\beta\mu_a^2}$$

Examples can be found of the closeness with which even this simplified formula represents many experimental results. Amongst the best of the published results must be included those obtained by J. Sameshima*

* Amer. J. of Science, Vol. XL., No. 10, p. 1482 (1918).

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for mixtures of acetone and ethyl ether. He himself assumes that these are really ternary mixtures of ether, acetone and tri-associated acetone, the molar fraction of the last named rising to as much as .5168 in pure acetone according to the law

$$\frac{(\text{normal mol.})^3}{(\text{assoc. mol.})} = \text{constant.}$$

PARTIAL PRESSURES OF ACETONE (A) AND ETHER (B) FROM A LIQUID MIXTURE.

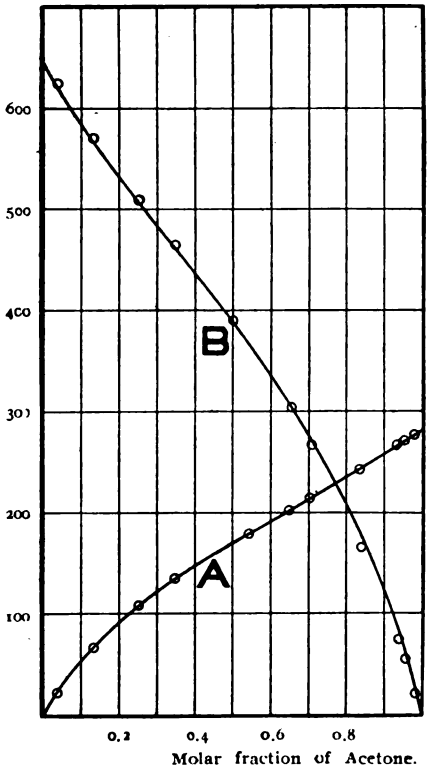

FIG. 3.

This case is interesting because the simplest form of the equation developed by Margules is capable of fitting the data equally well. This is shown in Fig. 3, and also by the following table:—

μ_a	π_a at 30° C. Exptl.	Calc.	μ_a	π_a at 30° C. Exptl.	Calc.
.03867	21.8	21.7	.7047	213.7	212.4
.1327	66.2	65.5	.8381	243.1	241.1
.2509	106.7	107.4	.9337	266.8	265.3
.3454	132.4	134.2	.9528	270.7	269.6
.4958	167.5	169.2	.9709	276.6	277.1
.6507	201.2	201.4	1.0000	282.7	282.7

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The above table gives the partial pressure of acetone calculated by taking $\beta = 0.7414$. The values for ether on the diagram (Fig. 3) are calculated from those for acetone by multiplying by 646/282.7 and plotting from the right-hand side of the figure as zero ($\mu_b = 0$) instead of from the left.

The agreement between theory and experiment is even closer than might have been expected; partly because only the simplest type of Margules equation has been employed and partly because the experimental values are calculated from the densities of the mixed vapours assuming the simple gas laws. [See Appendix.] Now for pressures reaching nearly to a whole atmosphere the assumption of the gas laws and the law of additivity which goes with them may be expected to break down. This is proved to be so by the determinations of molecular weight made by Sameshima from the vapour pressure of ether at different densities. These molecular weights rise gradually from 74.36 to 75.14 for pressures rising from 127.9 to 377.4, and for ether they rise from 57.99 to 59.06 for pressures from 56.7 to 174.3 mm. mercury.

A similar examination of a few of the experimental values obtained at 20° C. shows that at that temperature $\beta = .75$. Thus β increases slowly as the temperature is lowered.

Mr. Sameshima calculates a curve on the basis of the formation of tri-acetone in accordance with the law of mass-action. This curve also fits the experimental values very well.

This close fitting of the experimental data by means of two curves calculated from very different assumptions brings us into close contact with the controversy that has been engaged in by Dolazalek, who espouses the chemical view, and van Laar, who adopts the physical interpretation. A short summary of this controversy is given by F. H. Campbell (Trans. Farad. Soc., XI. 91, 1915). I have on more than one occasion emphasised the difficulty of distinguishing between these two theories. The Margules equation is equivalent to representing the deviation from the straight-line law on a molar fraction diagram as due to a differential attraction arising from the replacing some of the molecules of a substance by molecules of another kind. This mutual term would be of the form $\mu_a\mu_b$, so that the differential equation becomes

$$\mu_a \frac{d\pi_a}{d\mu_a} = a + b\mu_a(1 - \mu_a)$$

The second term on the right denotes a deviation from Raoult's law due to the presence of two types of molecules. It is akin to (and, in fact, represents) the term of the same kind in van der Waals' treatment of mixed gases. It can at best be only a first approximation to the effect of mixture. Now this product term suggests also the intrusion of a chemical change governed by the law of mass action. But this resemblance is more superficial than real, for if it be supposed to denote a reaction of the type

$$A + B \rightleftarrows C \qquad \text{(for example)}$$

then the term becomes $\dfrac{(\mu_a - x)\,(\mu_b - x)}{x} = \text{constant}$

where x is the amount of compound formed. Besides this remark, the following points are put forward for consideration:—

(a) The internal pressure which maintains a liquid in the liquid form is proportional to the square of the density for simple liquids.

When a mixture is made, product terms must enter representing the attraction of unlike molecules for one another. These must in

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general be present as long as the liquid form persists, and their effect must in every case be allowed for.

(b) Besides these, chemical changes (association, dissociation, combination) may also be present, and their effect must be allowed for. But the presence of these chemical changes is only occasional, and in any case their effect can only be allowed for in conjunction with the effect in (a), which is universally present.

(c) The small diminution of β with rise of temperature is consistent with what we know of molecular forces from gas behaviour and surface tension; it is inconsistent with the supposition of chemical change for which the variation with temperature is, in general, large.

The class of curves

$$\pi_a/\Pi_a = \mu_a e^{\beta(1-\mu_a)^2} \qquad)$$

is depicted in Fig. 4, each curve corresponding to a particular value

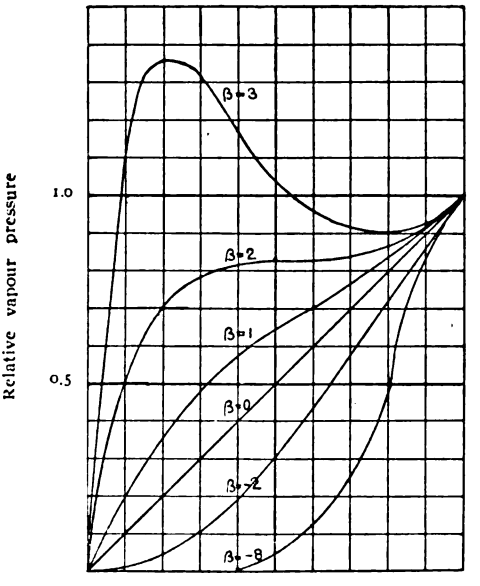

FIG. 4.

of β. These curves will enable the approximate value of β to be found by inspection for any particular vapour curve. The value of β may be either positive or negative. For $\beta=0$ the partial pressure line is a straight line. For positive values the curve lies wholly above the diagonal, for negative values it lies wholly below it. For $\beta=2$ there is a horizontal point of inflexion, and for higher values of β there are two points for which the vapour pressure is the same. This is of importance in connection with the equilibrium of partially miscible liquids.

The extent to which the physical interpretation by itself is capable of representing vapour pressures is shown further in Fig. 5. Comparison

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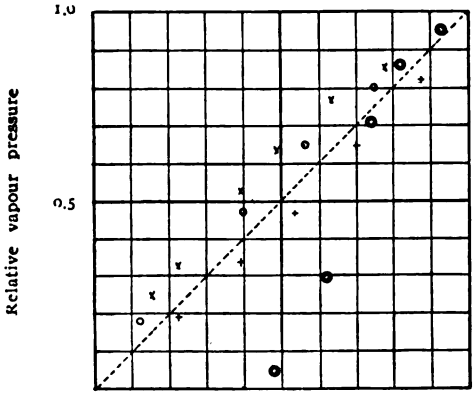
with Fig. 4 shows that for methyl-alcohol and glycerol $\beta = 1$ approx.; for acetone and oleic acid about 0.5; for ether and oleic acid about minus 0.2. The minus values mean that the attraction of the involatile substance on the volatile is more powerful than that of the volatile on itself, so that fewer molecules escape. The experimental data are from Campbell (loc. cit.).

It will be observed that the data for sulphuric acid-ether are partly below and partly above the diagram, and therefore they do not fit any of the curves on Fig. 4. In the lower part they fit $\beta = -6$ (approx.); there is no appreciable vapour pressure of ether until $\mu = 0.4$, and then the pressure rises quickly. When the mixture is nearly all ether there is an excess vapour pressure (i.e., curve is above the diagonal); this requires the sulphuric acid to be associated.



× Methyl alcohol and glycerol.
O Acetone and oleic acid.
+ Ether and oleic acid.
⊙ Ether and sulphuric acid.

FIG. 5.

It would appear that it is only in cases like this where the curves are of different character from those in Fig. 4 that it is safe to introduce the chemical hypothesis. At all events, in other cases the supposition is a superfluity.

APPENDIX.

The *exact* equation to replace the Duhem equation for a binary liquid mixture is:—

$$M_a v_a \frac{\partial \pi_a}{\partial M_a} + M_b v_b \frac{\partial \pi_b}{\partial M_a} - \left(M s_a + M_b \right) \frac{\partial p}{\partial M_a} = 0.$$

In the same way, if we do not wish to assume the gas laws for the vapour we must conduct similar cyclic operations on the vapour mixture and its separated components. If accented letters be used for the vapours we obtain

$$M'_a v_a \frac{\partial \pi_a}{\partial M'_a} + M'_b v_b \frac{\partial \pi_b}{\partial M'_a} - \left(M_a s'_a + M'_b s'_b \right) \frac{\partial p}{\partial M'_a} = 0.$$

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PART II.—EXTENSION TO SYSTEMS OF HIGHER ORDER.

The Duhem-Margules equation for a binary system is

$$n_a \frac{\partial \log \pi_a}{\partial n_a} + n_b \frac{\partial \log \pi_b}{\partial n_b} = 0$$

which, for increased brevity, we will write

$$n_a \frac{\partial l_a}{\partial n_a} + n_b \frac{\partial l_b}{\partial n_a} = 0.$$

In these equations n_a n_b are the numbers of *molecules* present.

By conducting the cyclic transformation in a different order we have also

$$n_a \frac{\partial l_a}{\partial n_b} + n_b \frac{\partial l_b}{\partial n_b} = 0.$$

This can be proved also by recognising that it does not matter which component we call *a* and which we call *b*.

If we differentiate the former equation partially with respect to n_b and the latter partially with respect to n_a we obtain

$$\frac{\partial l_b}{\partial n_a} = \frac{\partial l_a}{\partial n_b}.$$

But this is precisely the condition that l_b and l_a may both be derived from a single potential function; that is to say, from a function, P, whose first partial differential coefficient with respect to n_a is l_a and with respect to n_b is l_b.

For example, if we take the simple integral examined in Part I.

$$\pi_a = \Pi_a \frac{n_a}{n_a + n_b} e^{\beta \left(\frac{n_b}{n_a + n_b} \right)^2}$$

$$\pi_a = \Pi_b \frac{n_b}{n_a + n_b} e^{\beta \left(\frac{n_a}{n_a + n_b} \right)^2}$$

we easily obtain by integration

$$P = n_a \log \frac{n_a}{n_a + n_b} + n_b \log \frac{n_b}{n_a + n_b} + \beta \frac{n_a n_b}{n_a + n_b}.$$

This is the particular potential function required in the particular case. It will be observed that it is symmetrical with respect to n_a and n_b; and herein the advantage of using it will be found.

For it is quite easy to extend this new principle to systems of higher order than binary ones. In the case of a ternary system containing a third component, a cycle similar to the previous introduces a new diagram and a new term in the Duhem equation; and by conducting the cycle in different orders two similar equations are obtained. That is,

$$n_a \frac{\partial l}{\partial n_a} + n_b \frac{\partial l_b}{\partial n_a} + n_c \frac{\partial l_c}{\partial n_a} = 0$$

$$n_a \frac{\partial l_a}{\partial n_b} + n_b \frac{\partial l_b}{\partial n_b} + n_c \frac{\partial l_c}{\partial n_b} = 0$$

$$n_a \frac{\partial l_a}{\partial n_c} + n_b \frac{\partial l_b}{\partial n_c} + n_c \frac{\partial l_c}{\partial n_c} = 0.$$

By differentiating the first partially with respect to n_b and the second with respect to n_a and subtracting we obtain

$$\frac{\partial l_b}{\partial n_a} = \frac{\partial l_a}{\partial n_b}.$$

Similarly

$$\frac{\partial l_c}{\partial n_b} = \frac{\partial l_b}{\partial n_c}$$

$$\frac{\partial l_a}{\partial n_c} = \frac{\partial l}{\partial n_a}$$

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These three equations are the equivalent of the more complicated Duhem equations. Again, they represent the condition that l_a, l_b, l_c can be derived from a single potential function, P.

As for the original Duhem equation there is an undesirable indefiniteness about the information they give. But this is inseparable from the thermodynamic character of the principles on which they are based. Further data of a detailed mechanical kind are necessary before definiteness is secured. If, however, we limit ourselves at first to the potential which reduces to the previous value when *any one* of the components is absent (so that the system degenerates into a binary one) it is seen by inspection to be

$$P = n \log \frac{n_a}{n_a+n_b+n_c} + n_b \log \frac{n_b}{n_a+n_b+n_c} + n_c \log \frac{n}{n_a+n_b+n} + \frac{\beta_1 n_a n_b + \beta_2 n_b n_c + \beta_3 n_c n_a}{n_a+n_b+n_c}.$$

Hence by differentiating partially with respect to n_a, n_b, n_c in turn we obtain, if we write finally

$$\mu_a \text{ for } \frac{n_a}{n_a+n_b+n_c}, \quad \mu_b \text{ for } \frac{n_b}{n_a+n_b+n_c}$$

and

$$\mu_c \text{ for } \frac{n_c}{n_a+n_b+n_c},$$

$$\pi_a = \Pi_a \mu_a e^{\beta_1 \mu_b^2 + (\beta_1 - \beta_2 + \beta_3)\mu_b \mu_c + \beta_3 \mu_c^2}$$

$$\pi_b = \Pi_b \mu_b e^{\beta_2 \mu_c^2 + (\beta_2 - \beta_3 + \beta_1)\mu_c \mu_a + \beta_1 \mu_a^2}$$

$$\pi_c = \Pi_c \mu_c e^{\beta_3 \mu_a^2 + (\beta_3 - \beta_1 + \beta_2)\mu_a \mu_b + \beta_2 \mu_b^2}$$

The information which must be obtained from a mechanical theory or from experimental data is:—

i. The values of the three vapour pressures Π_a, Π_b, Π_c, for the components in a pure state.

ii. The values of the constants β_1, β_2, β_3.

If the data (i.) are known, then the values of β_1, β_2, β_3 can be derived from any three points on one or any of the partial pressure curves. The solution is perfectly easy, because the relations between β_1, β_2, β_3 are linear.

If we have studied the three possible *binary* mixtures formed from the three given components taken two at a time and have found that the corresponding simple equation holds good in each case and have found the values β_1, β_2, β_3 which then hold: these must also be the values of β_1, β_2, β_3 for the ternary mixture.

Some additional remarks seem called for in regard to the signification of this potential. Its existence implies that instead of expressing the state of the vapour in equilibrium with a given liquid mixture in terms of several dependent variables π_a, π_b, π_c, etc., we can express it in terms of one alone, viz., the potential P. This is completely analogous to the expression of three or more component forces in terms of a single potential when such exists: as it does in electrostatic problems.

The variables n_a, n_b, n_c are analogous to the co-ordinates of a point in three-dimensional space, and the values of $\log \frac{\pi_a}{\Pi_a}$ $\log \frac{\pi_b}{\Pi_b}$ $\log \frac{\pi_c}{\Pi_c}$ are analogous to component forces in these directions. The potential P then represents the work done in changing position in this space against the forces therein. Some hesitation may be felt in comparing the logarithms (which are mere numbers) to forces; and the values of n_a, n etc., to distances. Any difficulty should vanish when it is realised that

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in plotting n_a, etc., on a diagram we are always representing them by distances, and it is these distances on the diagram which denote co-ordinate positions.

The existence of a potential implies that there exists a function which undergoes no ultimate change in value if a cyclic series of positions is passed through; and this statement implies the validity of the three equations derived by me from the equations of the Duhem-Margules type.

The application to individual experimental investigations of this mode of obtaining theoretic values to the partial pressures of a mixture is deferred to a subsequent paper.

January 26th, 1920

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CONDUCTION OF ELECTRICITY THROUGH FUSED SODIUM HYDRATE.

By Alexander Fleck, D.Sc., F.I.C., and Thomas Wallace, M.Sc., A.I.C.

(*A Paper read before* The Faraday Society, *June* 14, 1920, Professor Alfred W. Porter, D.Sc., F.R.S., Vice-President, *in the Chair.*)

When the work described in this paper was commenced, its object was to determine the specific resistance of fused caustic soda. As the work progressed, however, its objective was altered, in view of the results obtained, and the above title shows that the scope has been considerably widened.

The paper limits itself to a description of experimental work, which may be conveniently divided into the several divisions indicated below:—

(1) Preliminary experiments with sodium hydrate solution.
(2) Resistance between two electrodes in fused sodium hydrate.
(3) Effect of altering the distance between electrodes.
(4) Effect of altering the size of electrodes.
(5) Change of resistance with temperature.
(6) Change of decomposition voltage with temperature.

1.—*Preliminary Experiments with Sodium Hydrate Solution.*

In the determination of the resistance of electrolytes as developed by Arrhenius, Kohlrausch and Nernst, according to well recognised laboratory methods, the use of vessels constructed from non-conducting material is invariably demanded. The shape of these vessels also requires to be clearly specified. We have been unable to trace

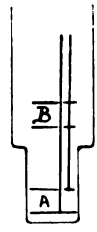

Fig. 1.

any reasoned explanation for the form of these vessels and electrodes, but a very simple experiment shows that this point is one of considerable importance. For instance, the actual resistance of a certain solution of sodium hydrate between two electrodes fixed relative to each other was determined by the standard laboratory method of Kohlrausch, with the usual form of glass vessel, as sketched in Fig. 1, position A. The electrodes were, of course, of platinum black and had a diameter just smaller than that of the narrow part of the vessel. The resistance was found to be 212 ohms. Without

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altering the position of the electrodes relative to each other, they were lifted into the broad part of the vessel, position B, and the resistance immediately fell to 60 ohms.

No very satisfactory explanation of the above phenomenon appears to be available, only very vague references to the effect of straying currents.

It is easily proved by actual experiment that if we have a column of solution in a glass tube and two electrodes which just fit into it, then the column of liquid has a resistance (measured by the standard Kohlrausch method), proportional to its length. This relationship holds, no matter whether the determination of the resistance is made by direct current or by the usual method of alternating current from an induction coil. The method of making the direct current determination is detailed later under paragraph 2. It is to be noted, therefore, that for an aqueous solution, before the resistance of the electrolyte becomes proportional to the distance between the electrodes, the electrolyte must be bounded by non-conducting walls, and that the area of the electrodes must be the same as the area of the column.

2.—*Resistance between Electrodes in Fused Sodium Hydrate.*

There is no substance available which is capable of withstanding the action of fused caustic soda for any length of time, and which is both non-porous and non-conducting.

It is, therefore, not possible to experiment with fused sodium hydrate in a confined space, and consequently all the methods and appliances for ordinary conductivity work are of little use in studying fused caustic soda. Other methods had, therefore, to be used. Since the vessel for containing the fused material was of iron, it was decided that the best method of working was to use a large bulk of material, so that the experiments could be carried on in the centre of it, well out of any influence that the conducting walls could possibly have.

An iron vessel, in the form of an inverted cone, was therefore used, which was four feet deep and four feet in diamter, and which held nearly a ton of molten caustic soda. If two electrodes are immersed in the centre of such a mass of molten caustic, and the measurement of resistance of soda between the electrodes attempted by means of a Wheatstone Bridge arrangement, with alternating current from a conduction coil, and a telephone in place of a galvanometer, no results are obtained on account of the following reasons:—

(a) The impossibility of obtaining a silent point, due mainly to the type of electrodes which must be used. It is not possible to use electrodes of platinum black, as is demanded for this type of work generally.

(b) The resistances to be measured are so small, 0.2 ohms being about the largest ever experienced.

It was decided, therefore, to work with electrodes immersed in a large quantity of fused soda, and in the first experiments direct current was used. The electrodes were made of sheet nichrome 0.076 cms. thick, and the general method was to pass varying currents between the electrodes and measure the corresponding voltage drops, the current being varied from 0.5 to 5 amps. as a rule.

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When plotted, these points lay on a straight line, except at very low currents, and by producing this line until it cut the zero amps. line, the decomposition voltage was obtained. By subtracting this decomposition voltage from the voltage corresponding to a particular amperage, the resistance could then be calculated from Ohm's Law. An example of the curve so obtained is shown in Fig. 12.

The apparatus used was as follows:—

The electrodes were rectangular pieces of nichrome, with stems about 20 cms. long, also of nichrome. These electrodes were 2.54 cms.

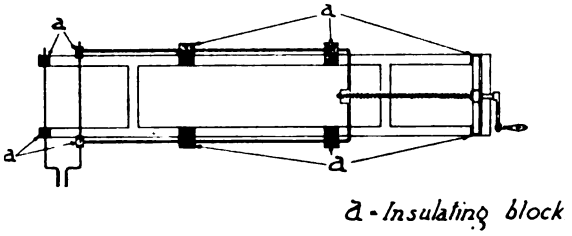

FIG. 2.

deep, and were of various widths, from 0.3 cms. to over 10 cms. They were always immersed to the beginning of the stem.

The most important part of the apparatus was the electrode holder. Various types were used, but the form found most convenient is sketched in Fig. 2. The electrodes could easily be removed and replaced, when necessary, by others.

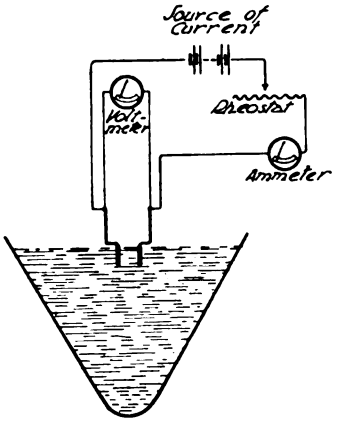

FIG. 3.

The whole arrangement was suspended by a slow moving block and tackle over the soda, and the depth to which the electrodes were immersed could be accurately adjusted.

The containing vessel was heated by an oil burner, and the temperature of the soda recorded by a thermograph. In general the working temperature was 360°.

The electrical connections were, therefore, quite simple, and are sketched in Fig. 3.

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3.—*Determination of Resistance when the Distance Between Two Electrodes is Altered.*

A pair of electrodes, each of dimensions 2.54 × 2.54 cms. square, were fixed to the apparatus, and were immersed in molten sodium hydrate and a series of volts-amps. curves obtained for them at various distances; the decomposition voltage was thus obtained from a number of curves. The electrodes were then brought close together, and a constant current of four amps. allowed to flow between them. The by putting a fine piece of "eureka" wire in parallel with the electrodes.

TABLE 1.

Current: 4 amps.

Resistance.	0.018	0.026	0.035	0.0425	0.054	0.067	0.079	0.084	0.093	0.095
Distance. cms.	0.1	0.28	0.5	1.1	1.4	2.25	3.8	4.4	6.1	7.3
Resistance.	0.099	0.101	0.102	0.105	0.1035	0.104	0.105	0.105	0.104	
Distance. cms.	9.1	10.4	12.2	13.7	14.45	15.0	16.1	18.1	18.4	

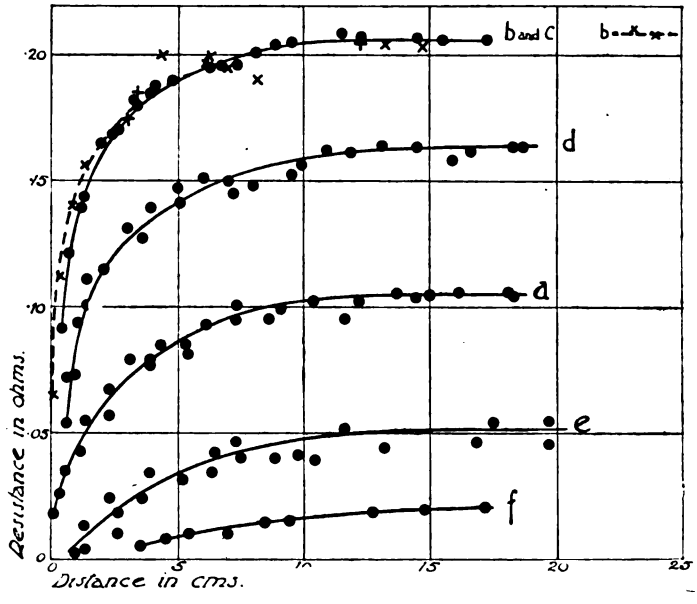

FIG. 4.

between them. The latter was then increased by successive short steps, until it was altered from its initial value of 1 mm. to a final value of 20 cms. The actual resistance in ohms can then be calculated.

Table 1 shows the results obtained, and when plotted they give curve (a), Fig. 4.

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This series of determinations was carried out with the use of five other electrodes of the dimensions 2.54 × 0.317, 2.54 × 0.635, 2.54 × 1.27, 2.86 × 6.04, and 2.86 × 10.17, and the curves obtained are plotted in Fig. 4, curves b and c, d, e and f.

They show that as the distance increases the rate of increase of resistance is large initially, as a rule, but rapidly falls off, and finally an increase of distance between the electrodes does not produce any increase of resistance. This is a result of considerable importance. It has also to be noted that with small electrodes the initial rise is much steeper than with large electrodes.

In addition to the figures given above, extreme cases have been tested where the electrodes were about 1 metre apart, and yet the

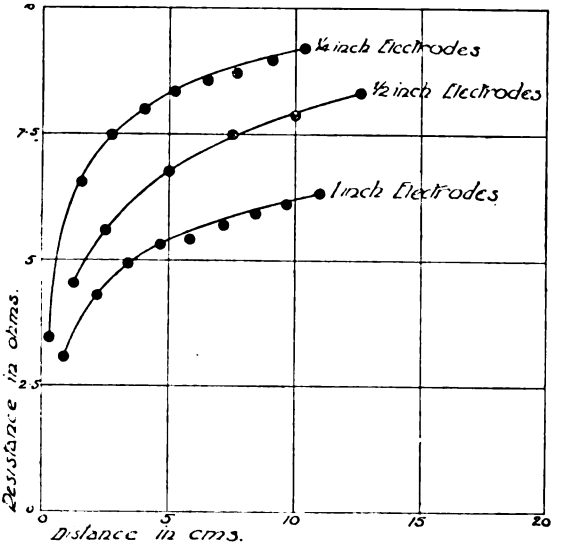

FIG. 5.

resistance was no greater than when the electrodes were 15 cms. apart.

It is well to point out that the conductivity of aqueous solutions does not behave analogous to the experiment described above.

Fig. 5 shows curves obtained when electrodes are similarly immersed in an aqueous solution and the distance between them gradually increased. It is seen that the resistance between two electrodes increases continually with increasing distance. Conclusions, therefore, which are drawn from the experimental work on fused caustic are therefore not applicable directly to the conduction of electricity through aqueous solutions. These experiments with fused caustic have also been performed in vessels of other shapes, and have been shown to be independent of the form of container.

It should be noted also that when the electrodes are so far distant that an increase does not demand an increase of voltage, then the relative position of the electrodes to one another has no influence on the voltage necessary to maintain a given current.

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This was shown by immersing the electrodes of size 10.17 × 2.86 cms. to the standard depth at about 23 cms. apart. One electrode was then revolved about its stem through a complete circle, while the current was passing. No variations were observed in either the voltage or the current throughout the complete revolution.

3.—*Effect of Altering the Distance Between Electrodes When Alternating Current is Used.*

Similar experiments were made with alternating current. For these experiments current was generated by a Crypto variable frequency generator with a maximum output of 350 watts. The ammeter used was a hot wire instrument, and the volts were measured by putting a fine piece of "Eureka" wire in parallel with the electrodes.

TABLE 2.

Alternating Current

Resistance	0.087	0.1045	0.1135	0.119	0.1245	0.129	0.1325	0.135	0.135	0.135
Distance cms.	0.5	1.1	1.6	2.5	3.4	4.65	6.2	8.2	10.9	14.2

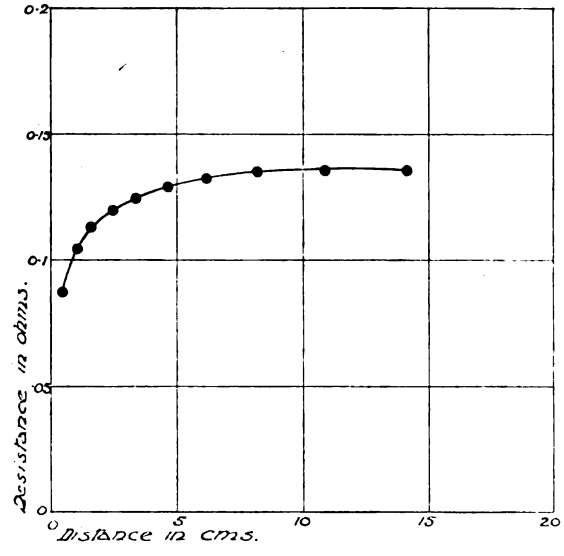

FIG. 6.

A thermocouple of equally fine copper and eureka wires were soldered on to the first wire. This instrument was calibrated by passing a direct current through the wire. The drop in voltage between the two ends was measured by a standard millivoltmeter, and at the same time the deflection obtained on a mirror galvanometer connected with the thermocouple was noted. In this manner a calibration curve was obtained.

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When alternating current was being used, the deflections obtained on the mirror galvanometer were noted, and from the calibration curve obtained above, the corresponding voltage was obtained. In this experiment the current was maintained constant at 5 amps., and the electrodes were of dimensions 4.5 × 1.1 cms. The following results were obtained (Table 2), and the corresponding curve is shown in Fig. 6. It is seen that it is similar in every respect to the curve obtained for direct current, and it is to be noted that the resistance above which no increase is obtained is the same as would have been obtained if direct current had been passed by means of the same electrodes.

4.—*Effect of Altering the Size of Electrodes.*

It is seen from Fig. 4 that with small electrodes the final resistance between them varies but slowly. As, however, the electrodes are larger, the final resistance is much smaller. Some experiments were made which throw some light on the way in which the size of the electrodes alters the final resistance.

On account of the fact already mentioned, namely, the impossibility of obtaining walls which are non-conducting, but would stand up to fused caustic soda, experiments were first of all carried out in aqueous sodium hydrate solution.

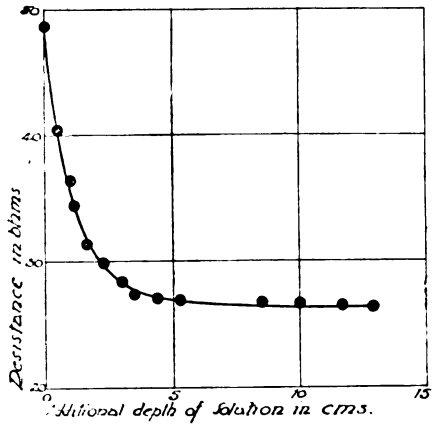

FIG. 7.

Caustic Soda Solution.

A rectangular glass jar was taken, of dimensions 3.1 × 7.4 × 16 cms., and two electrodes of 3 cms. long by 2.86 cms. high were placed at the bottom against the 3.1 cms. sides of the vessel, and were thus at a distance of 7.2 cms. The solution was then put into the vessel until the top of the electrodes were just covered. The resistance between the electrodes was then measured, and the successive additions of 50 cms. of solution were made until the vessel was filled, each addition raising the level 0.65 cms. Between each addition the resistance was determined. The curve obtained is shown in Fig. 7,

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and it will be noticed that the resistance ceases to fall when the depth of liquid has been raised beyond the length of the electrodes by 3.7 cms.

The total breadth of the liquid is 7.2 cms., so that the resistance remains constant after enough solution has been added to allow a semi-circle erected on a line joining the top of the two electrodes to be entirely within the liquid. This experiment has been repeated with glass vessels of other dimensions.

A similar rectangular vessel was completely filled with the same solution, and similar electrodes placed in a vertical plane against the sides of the vessel, as low down as possible. The resistance was determined, and then the electrodes were raised in small steps, until their top edges were on a level with the surface of the liquid. Between each step the resistance was determined. The curve obtained is shown in Fig. 8. The electrodes were 12.2 cms. apart, and it is

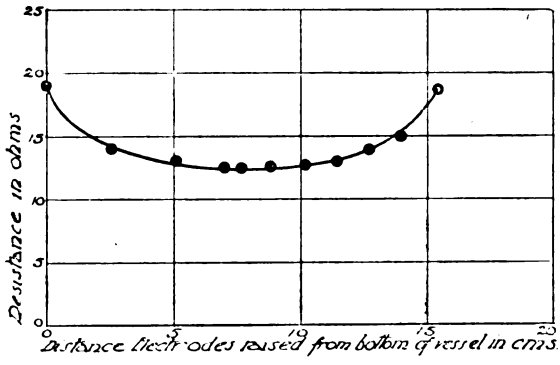

FIG. 8.

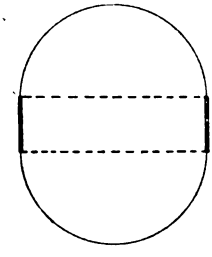

FIG. 9.

seen that there was practically no change in the resistance after the electrodes had been raised 6.2 cms., and until the top edges were 5.7 cms. from the surface of the liquid.

Again, it is seen that so long as semicircles erected on the lines joining the top edges or the bottom edges of the electrodes be wholly within the liquid the resistance does not vary. If either of these semicircles cannot be completed owing to the walls of the vessel, then the resistance increases. This experiment has been confirmed in different vessels with similar electrodes.

These two experiments suggest that the path of the current between two electrodes placed in a large quantity of electrolyte at a given short distance apart extends throughout the quantity of material bounded by spherical surfaces erected on the edges of the electrode and lying in the electrolyte.

This means that if we take a section at any angle through the electrodes, the section of the mass of electrolyte involved in carrying the current is as shown in Fig. 9.

Experiments were now carried out in sodium hydrate solution, similar to those for fused caustic soda, from which Fig. 4 was obtained.

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The results have been already shown in Fig. 5, and the first point to notice is that the same phenomenon is not seen with an aqueous solution as with fused sodium hydrate. It is observed that with an increasing distance the resistance between two electrodes continues to increase.

It is, therefore, to be remembered that deductions made from observations of phenomena with aqueous solutions must be applied with great care to results of experiments with fused caustic.

From these curves it is possible to test the volume hypothesis just put forward. If this is correct, then at a given distance the resistance must vary inversely with the volume, *i.e.*, R × V = a constant.

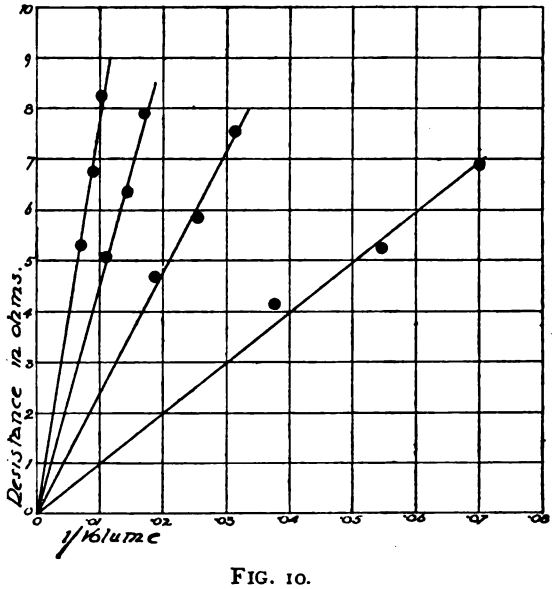

FIG. 10.

Table 3 shows the figures worked out for various distances, and in view of the number of uncertainties, the approximately constant value obtained for any given distance up to 5 cms. apart is considered satisfactory. We may thus come to the conclusion that the volume hypothesis just put forward for aqueous solution approximates in a fair measure to the truth. It is to be noted, however, that after 5 cms. this relation does not hold.

The result is also shown graphically in Fig. 10, where it is seen that we get a straight line passing through the origin if we plot the resistance against the reciprocal of the volume.

We have now to enquire whether this relation holds for fused caustic soda.

Table 4 shows the data obtained for fused caustic from Fig. 4, collected similarly to Table 3, and it is at once seen that the volume × resistance is by no means constant. If, however, we plot the resistance against the reciprocal of the volume we again get straight

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TABLE 3.

Distance.	Dimension of Electrode.	Volume.	Resistance.	Vol. × Res.	1/Volume.
2	2.64 × 2.54	26.90	4.15	107.0	.0372
2	2.54 × 1.27	18.33	5.25	96.4	.0545
2	2.54 × 0.635	14.28	6.9	98.54	.07
3	2.54 × 2.54	53.34	4.7	250.75	.01875
3	2.54 × 1.27	39.17	5.85	229.1	.0255
3	2.54 × 0.635	32.10	7.55	242.25	.03115
4	2.54 × 2.54	90.31	5.05	456.1	.01108
4	2.54 × 1.27	69.45	6.35	441.2	.0144
4	2.54 × 0.635	59.01	7.9	466.2	.0168
5	2.54 × 2.54	139.72	5.3	740.5	.00715
5	2.54 × 1.27	111.13	6.75	750.0	.00899
5	2.54 × 0.635	96.84	8.25	799.2	.0103
6	2.54 × 2.54	200.2	5.45	1091.5	.00498
6	2.54 × 1.27	163.3	7.0	1143.0	.00612
6	2.54 × 0.635	144.9	8.45	1225.0	.0069
7	2.54 × 2.54	281.9	5.65	1592.5	.00355
7	2.54 × 1.27	234.8	7.3	1714.0	.00425
7	2.54 × 0.635	211.3	8.6	1818.5	.00474

TABLE 4.

Distance.	Dimensions of Electrode.	Volume	Resistance.	Vol. × Res.	1/Volume
2	2.835 × 5.98	54.03	.02	1.096	0.0185
2	2.54 × 2.12	26.96	.065	1.695	0.0371
2	2.54 × 1.27	18.33	.118	2.175	0.0545
2	2.54 × 0.635	14.28	.159	2.2	0.07
2	2.54 × 0.317	12.27	.167	2.05	0.0815
3	2.835 × 5.98	99.20	.028	2.78	0.0101
3	2.54 × 2.54	55.34	.072	3.84	0.01874
3	2.54 × 1.27	39.17	.128	5.01	0.0255
3	2.54 × 0.317	28.56	.18	5.14	0.035
4	2.835 × 5.98	157.6	.035	5.52	0.00634
4	2.54 × 2.54	90.31	.08	7.22	0.01109
4	2.54 × 5.27	60.45	.136	9.44	0.0144
4	2.54 × 0.635	59.01	.186	10.98	0.0169
4	2.54 × 0.317	53.80	.189	10.17	0.0186
5	2.835 × 5.98	231.65	.038	8.8	0.04315
5	2.54 × 2.54	139.72	.0826	12.0	0.00716
5	2.54 × 1.27	111.13	.142	15.77	0.00899
5	2.54 × 0.635	96.84	.191	18.5	0.0103
5	2.54 × 03.17	89.69	.195	17.5	0.01115

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lines, but they do not go through the origin. It is difficult to see exactly what the interpretation of these curves is, but it is obvious there are complications by factors not yet determined. The curves are shown in Fig. 11.

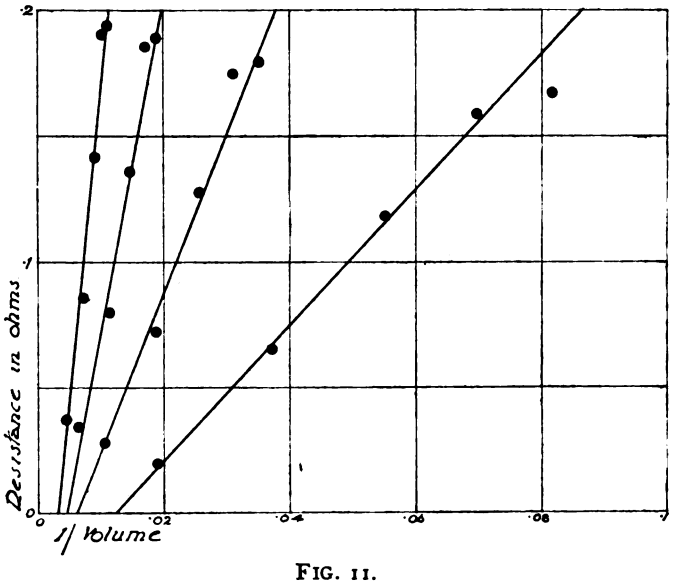

FIG. 11.

5.—*Change of Resistance with Temperature.*

In the course of the work on distance, an opportunity was taken to find out what the influence of temperature was on the resistance between two terminals. For this purpose two electrodes were immersed in the mass of fused soda, and its temperature was maintained at this point until a volts-amps. curve was obtained. Such a curve was repeated for every 40°, and in this way the decomposition voltage was obtained. If we now take the necessary voltage for 5 amps., we get the following table (Table 5), from which the resistance can be calculated.

This gives the result when using electrodes of 4.5 × 1.1 cms., that the resistance decreases 2.04 × 10 ohms per degree C. rise of temperature. This is equivalent to a fall in resistance per degree C. rise of temperature of 0.102 per cent. In this calculation the value of the decomposition voltage is very important, and it is interesting to note that if Neumann and Bergve's value is assumed to be correct (*c. f.* page 357), the resistance of fused caustic actually increases with increased rise of temperature. As will be pointed out, however, our own value for the rate of change of the decomposition voltage with temperature is considerably different, and assuming that it is correct, the rate of change of resistance is shown to be quite in line with the well-known fact that resistance of aqueous solutions falls with rise of temperature.

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6.—*Decomposition Voltage.*

As the value of the decomposition voltage was often being required, an enquiry was made into its general behaviour. The mass of soda was maintained at various temperatures between 320° and 480° C. At each temperature direct current was passed between two electrodes of nichrome, and the voltage necessary for various currents to pass

TABLE 5.

Temp	Current	Total Voltage	Decomposition Voltage	Voltage to overcome Resistance	Resistance
480	5	2.844	1.952	.892	.1784
440	5	2.972	2.00	.972	.1944
400	5	3.124	2.16	.964	.1928
360	5	3.248	2.236	1.012	.2024
340	5	3.336	2.308	1.028	.2056
320	5	3.388	2.332	1.056	.2112

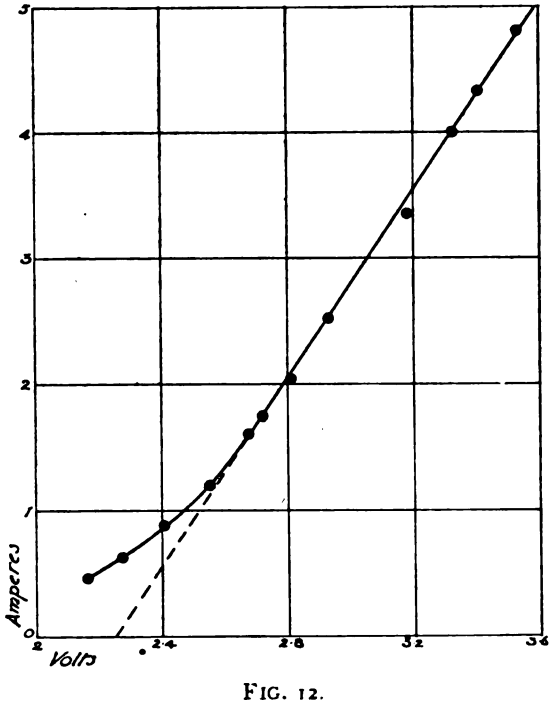

FIG. 12.

determined. The curves obtained were produced until they crossed the zero amps. line, and the value of the voltage thus obtained is the decomposition voltage. In this way it was found that the decomposition voltage was a variable quantity, which diminished as the temperature rose. This result was obtained independently of, but subsequent to, the publication of a paper by Neumann and Bergve.*

* Neumann and Bergve—*Zeitsch fur Elektrochem.*, 1915, *21*, 143.

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We agree with their general conclusion, but we find that the coefficient is 2.25×10^{-3} for each degree C. rise in temperature, in place of 2.95×10^{-3} given by them.

The actual value of the decomposition voltage has been found to vary between 1.952 volts at 480° C. and 2.332 volts at 320° C., as shown in Table 5.

Fig. 12 shows a volts-amps. curve for a temperature of 380°, and it will be noticed that as the volts approach the zero value the curve ceases to be a straight line, and the amps. carried become greater than we would expect. This comparatively well-known effect is ascribed to the presence of water in the molten caustic, and for the purpose of the determination of the decomposition voltage this portion of the curve was neglected.

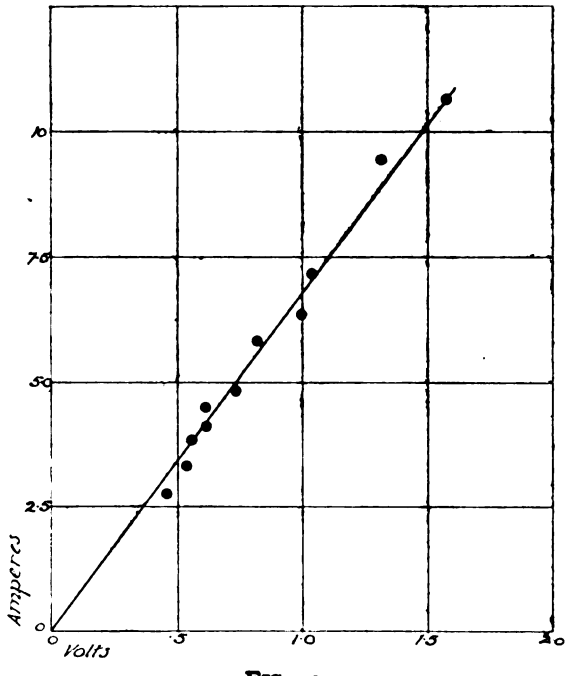

FIG. 13.

In all literature on this subject it is customary to speak of the decomposition voltage as a characteristic property of caustic soda. It should be noticed, however, that if electrodes of metallic sodium are used, the volts-ampere curve goes through the origin. The method of carrying out this experiment was to arrange two copper connections over the surface of the soda and to support round each of these two cylindrical pieces of gauze. The circuit was then completed by dropping into the molten soda pieces of sodium until connection was made between the copper and the soda. When this had been done, then a variable current was passed and the corresponding voltage measured for each amperage.

The curve is shown in Fig. 13, and it is seen that it passes through the origin, showing that Ohm's Law holds under these conditions. The

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conclusion to be drawn from this experiment is, of course, that no energy is required to commence ionisation, which confirms for fused sodium hydrate the view already held almost universally for aqueous solutions that ions are always initially present in an electrolyte.

Summary of Results.

The result of this work given above may be summarised as follows:—

(1) It has been shown that if a constant current is passed between two electrodes placed closely together immersed in a mass of fused caustic soda, and the two electrodes are moved apart, then the resistance increases until a certain maximum value is reached, after which it remains constant.

(2) The conduction of electricity across fused caustic soda by electrodes of different sizes has been studied, and an approximate idea has been obtained of the laws which govern the rate of change of resistance compared with the size of the electrodes.

(3) The rate of change of resistance between 320° C. and 480° C. for fused caustic has been found to be 0.102 per cent. fall per ° C. rise in temperature.

(4) The decomposition voltage has been studied, and has been found to be a variable quantity, decreasing at the rate of 2.25×10^{-3} per ° C. rise in temperature. This figure is considerably different from Neumann's figure of 2.95×10^{-3}

(5) A current has been passed through fused caustic soda between two sodium electrodes. It is found that Ohm's Law is obeyed, so that we have here a confirmatory experiment that in fused caustic soda ions are already in existence, and that no energy is required to disrupt the molecule of sodium hydrate.

We desire in conclusion to acknowledge our indebtedness to the Directors of the Castner-Kellner Alkali Co., Ltd., for the facilities which were available in their Wallsend Works. Our thanks also are due to Mr. W. W. Marshall for his help in carrying out some of the practical measurements, and to Mr. H. Parry for his suggestion for the method of measuring the small alternating current voltage.

16th December, 1919.

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Discussion.

At the conclusion of the reading of the paper,

Dr. Fleck said he had given a résumé of the paper which had been accepted by the Faraday Society for publication, but it differed from the paper which had been sent in by the authors. They regarded the curves shown in Fig. 4 as of considerable importance and worthy of consideration, and as they had a rather undefined feeling that conduction through aqueous electrolytes was to be regarded as the normal type, and as they found that the fused electrolyte was different from the aqueous one, they offered what they were careful to call a suggested explanation. The Publication Committee of the Faraday Society, however, said that the curves were merely what was to be expected, and that no explanation was required. The Committee referred the authors to the fact—worked out for conduction through metals where there were two point electrodes for conveying current through a metal sheet of which the boundaries were at an infinite distance—that conduction took place along tubes which were narrow near the electrodes but became relatively very wide between them. Consequently it was concluded that by far the greater part of the resistance was in the neighbourhood of the electrodes and that altering the distance would make very little difference in the resistance to the current flowing between them. The Committee had therefore struck out the portion of the paper dealing with the suggested explanation. In reply to that argument, the authors had to say that they were not dealing with metallic conduction at all. They were already aware that a curve somewhat similar was obtained when similar measurements were carried out in the case of the one metal they had tried, viz., mercury. So far as the authors' experiments went, however, they found that the curve did not become quite horizontal, but that there was a continual, though small, increase in resistance as the distance between the electrodes is increased. They were therefore of opinion that in carrying out experiments with fused caustic soda, with an aqueous solution of caustic soda and with mercury, three distinct phenomena were observed, viz., that the curve with caustic soda went up and then became horizonal, that the curve with aqueous caustic soda went up and then slowed off somewhat, but still went on rising, and finally the curve for mercury showed a very small but still definite increase in resistance as the distance was increased. The authors' first point in reply, therefore, was that the experimental evidence did not support the view that because certain reasoning applied to metallic conduction the same reasoning would apply to conduction through fused caustic soda. The second point was that conduction through metal was distinctly different from conduction in electrolytes. From the theoretical point of view, one condition which held in the case of metallic conduction was that there was molecular uniformity throughout. In the case of conduction through fused

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caustic soda there was no such uniformity. The authors were therefore of the opinion that because one conclusion might be accepted for metallic conduction, it did not follow that the same conclusion could be accepted in the case of conduction through fused caustic soda.

In a further remark, Dr. Fleck said that Mr. Wallace and he were not endeavouring to show that Ohm's law did not hold. It would be seen from the paper that they depended on it for the calculation of the resistance.

Professor A. O. Rankine: The authors claim to have discovered a difference in the mode of electrical conduction in fused sodium hydrate as compared with an aqueous solution of the same substance. This is so surprising a result that it cannot be accepted without careful examination of the experiments on which it is based. There are certainly differences between the two sets of curves indicated in Figs. 4 and 5 respectively. But these curves appear to have been obtained from experiments carried out in vessels very different in size and material, and this factor throws grave doubt on their comparability.

Experiments in sea water in which I was interested some time ago gave results quite at variance with the authors' view. The resistance between two electrodes immersed in sea water was found to become independent of their distance apart as soon at that distance was made large in comparison with the dimensions of the electrodes. This is, of course, completely in accordance with the ordinary theory of current flow, whether in metals or electrolytes, provided that the conductor is practically infinitely extended. The same result has been found by the authors in the case of fused caustic held in a very large container, and their observation that at considerable distances apart the orientation of the electrodes has no effect on the resistance between them is also precisely what is to be expected according to ordinary theory. It seems impossible to resist the conclusion that the difference between fused caustic and solution has not been really established, and that the failure of the curves in Fig. 5 to become horizontal is to be attributed to the smallness and material of the container.

Dr. H. F. Haworth, before reading his own paper, said that he had wanted to say something with regard to the last paper, and thought he would leave it until he came to read his own.

There was a rather startling admission on the first page of Dr. Fleck's paper, where it was stated that the authors tried to measure the resistance of the soda between the electrodes by means of a Wheatstone bridge, but apparently they gave it up.

He had not seen the paper before that evening, but it seemed to him that it was an extraordinary thing that they could measure the resistance by means of the ammeter-voltmeter method, but that their bridge arrangements were so poor that they could not obtain any results by these methods. He knew very little about chemistry, and was simply looking at the matter from the electrical measurement standpoint. If they took an electrolytic cell, and put it in a bridge,

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it appeared as a capacity C in series with a resistance R. When they came to low resistances with electrodes of small capacity, they were in trouble immediately with the ordinary chemical method of measuring resistance, because the current was considerably out of phase with the applied voltage, and it was impossible to obtain a balance on the bridge with resistance only. The reactance of the cell must be balanced by a corresponding reactance in the bridge, and the apparent resistance of the electrolytic condenser must be subtracted from the apparent resistance of the cell, in order to obtain the true resistance of the liquid between the electrodes.

Chemists tried to get over their difficulties by making $RC\omega$ large (where $\omega = 2\pi$ *frequency*), but this was not always possible or desirable. In these cases one or other of the methods outlined in the paper following should give satisfactory results.

The Chairman said there were two sides from which this paper might be viewed. One was that it was a piece of experimental investigation which would prove of use to those engaged in technical practice involving conduction through large quantities of such a substance as fused sodium hydrate, and he thought the authors were to be congratulated upon having made some very careful experiments in that direction. The other side of the question was as to the interpretation of the results obtained. The great point in the paper, as he understood it, was to put forward an essential distinction between the mode of conduction in fused soda and the mode of conduction in electrolytes, or, at any rate, a distinction between conduction in fused soda and conduction in metals. First of all, it had been shown by Trouton and FitzGerald, working together, that Ohm's law held good in the case of electrolytes, and therefore they must expect in the case of electrolytes the same phenomena that were obtained in the case of conduction in metals. In the latter case there is no doubt whatever what happens, and so many of the results obtained by the authors had a rough resemblance to those obtained in the case of conduction in metals that until the matter was investigated more fully he thought they must feel that there was probably some connection between the two. It must be stated at once that there were some apparent differences between them so far as the experiments were concerned, but then there were differences in the experimental conditions—differences in the size of the apparatus, in the size of the pots used, and so on. All such points as these must be taken into consideration before we could feel very sure that there was any distinction at all between the two kinds of conduction, viz., that in soda and in an electrolyte or that in metals. The first experiment, for example, represented in Fig. 1, gives precisely the kind of result that would be expected in the case of ordinary conduction in a metal. In the first place, when the electrodes were in the position A, the lines of flow of current were parallel lines. The wall of the vessel served as a kind of guard ring, preventing the current spreading outwards. Provided they assumed the flow to be exactly along straight lines, then the resistance would be precisely proportional to the distance between the electrodes, and that was what the authors obtained. On the other hand, when the electrodes were moved out into the expanded parts of the vessel,

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the flow was quite different, because not only could the current pass straight across between the electrodes, but it spreads out sideways as well. The lines of flow have, in fact, the same shape as for a parallel plate condenser. As to how much spreading out could occur depended upon the relative magnitudes of the electrodes, the size of the vessel, and the distance between the electrodes. If we vary any one of these three quantities some variation will be produced in the resistance between the electrodes. It would need very careful working out in each specific case before we could say exactly what the influence might be. There are certain difficulties in working out problems of this kind where there are irregular conductors to deal with. The mathematics of the problem did not suit at all the physics, and it was only possible to get an idea of what was likely to occur by making certain approximations. We might take, for instance, two cylindrical conductors in a cylindrical vessel, and with a little trouble we can work out the result which might be expected. The result would be very much the same as that which Dr. Fleck obtained. At any rate, there was so little difference between the two, that it cannot be considered strong evidence in favour of the breaking down of Ohm's law. He confessed that he rather felt that Ohm's law held throughout, though it might be admitted that there might be some complication in the case of fused sodium hydrate which did not occur in the case of electrolytes. The proof that that was so required to be made stronger before it was likely to be accepted.

On the whole, the paper gave the results of some very careful work, and it should be of great use to those engaged in technical practice. It was well that attention should be drawn to the matter. Probably it was not generally known what the general properties of conduction in electrolytes were, and so it was useful to call attention to them. Professor Rankine had already said that this was the kind of calculation employed in practice in similar cases. It has also been employed in calculating the resistance of cells like the Daniell cell, consisting of one cylindrical electrode inside another, and the results fitted in with practice.

The question is very fully discussed in Mascart et Joubert, *L'Electricité et le Magnetisme*, I. pp. 238, etc. They show that for spherical electrodes of radius r *small compared with their distance apart* the total resistance R equals $1/(2\pi kr)$ where k is the electrical conductivity, and they add, it is remarkable that the resistance is independent of the distance between the electrodes, and only depends upon their dimensions and the conductivity of the medium. The case for cylindrical electrodes is worked out completely (but more simply) in Foster and Porter, *Elementary Treatise on Electricity and Magnetism* (1913), p. 195. It is there applied to the case of the flow through a cell such as a Daniell's cell with cylindrical electrodes. The Chairman had occasion during the war to apply it to the case of large iron pots containing acid mixture in which an aluminium rod was immersed, and satisfactory correspondence was obtained between the calculated resistance and the current actually measured.

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Fused salts have previously been examined by Bouty and L. Poincaré* using non-polarisable electrodes. They find that in every case the conductivity increases with rise of temperature; Dr. Fleck confirms this for fused sodium hydrate.

Dr. Fleck, replying to the discussion, said that both Mr. Wallace and himself thoroughly agreed with the Chairman in regard to Ohm's law. They were not trying to call Ohm's law into question at all.

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* Ann. de Chim. et de Phys. 6,t. xvii, 1889.

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THE MEASUREMENT OF ELECTROLYTIC RESISTANCE USING ALTERNATING CURRENTS.

By H. F. HAWORTH, PH.D., M.Sc., B.ENG., M.I.E.E.

(*A Paper read before* THE FARADAY SOCIETY, *June* 14, 1920, PROFESSOR ALFRED W. PORTER, D.Sc., F.R.S., VICE-PRESIDENT, *in the Chair*.)

Contents.

(1) Apparatus.
(2) Methods of measurement.
(3) Dilution experiments with KCl, using platinised and non-platinised electrodes.
(4) Impedance—Frequency locus for an electrolytic cell.
(5) Resistance—Frequency results from chlorides of K, Na, NH_4, Fe, Ni, and Co.
(6) Resistance and capacity changes with temperature.
(7) Potentiometer measurements.
(8) Summary of results.

If an alternating current is sent through a solution, and the electrical constants of the apparatus between the current carrying electrodes are determined, the cell appears as a capacity in series with a resistance. If the values of capacity and resistance are determined at various frequencies, they will be found to vary with the frequency.

The following experiments were made in order to see what relation existed between the apparent resistance of the cell, as measured between the current carrying electrodes, and the true resistance of the electrolyte as determined by other methods.

A method is experimentally deduced showing how the true conductivity of a strong solution can be obtained from the variation of the apparent resistance with frequency, when it is measured in a low resistance cell, using plain platinum electrodes.

No bridge measurements of electrolytic resistance which only give minimum balance, such as are in general use, can be accepted as satisfactory. If we are actually measuring a definite resistance it should be possible to do so with zero balance on a bridge.

Apparatus.—The first thing to be done was the production of suitable apparatus for the experiments.

In measurements dealing with capacity and self-induction it is desirable to adopt a sine wave of E.M.F., as many formulae employed presuppose such a wave shape, and with it the current in a circuit containing capacity can be brought exactly into phase with the voltage across it by the introduction of a suitable inductance, the conditions being that $\sqrt{\text{C.L.}} = \frac{1}{2\pi f}$. The current is then not only in phase with the applied voltage, but has the same wave shape, namely sinusoidul.

The Alternators.—For the production of this sine wave E.M.F. after a considerable amount of experimenting two machines were designed and constructed, having their armatures connected directly on to the shaft of the motor driving them. This

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gave a smooth drive without any backlash or oscillation such as would be caused by any flexible coupling or belt drive. This is a very important point—constancy of supply frequency—when dealing with A.C. measurements involving the use of a vibration galvanometer and where mixed circuits containing capacity and self-induction are being dealt with, as alteration of frequency produces alteration of balance and alteration of galvanometer sensibility. The alternators were provided with six poles and 24 poles respectively, and were combined with $\frac{1}{4}$ h.p. Siemens-Schuckert motors, which could be run up to a speed of 5,000 R.P.M., giving maximum frequencies of 250 and 1,000 cycles per second. The armature of the 250 frequency machine was a smooth ring, and had a simple ring winding on it covering the whole of the armature. The armature of the 1,000 fre-

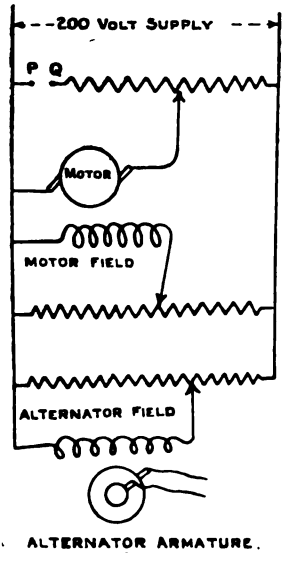

FIG. 1.

quency machine was also a smooth ring, but has former wound coils simply placed on the surface and held in position by steel binding wire. The original winding was single phase, covering half the armature, but recently another phase has been added similar to the first, giving an increased output, also a two-phase supply. The field coils are only wound on every other pole, the coils completely filling up the winding spaces between the poles, giving the effect of a wave winding on the field. This machine has proved extremely satisfactory for all kinds of alternating measurements, and is such that it could be easily constructed in any electrical workshop, or could be turned out at a moderate price by constructors of small machines.

A speed indicator is attached to each machine to give the frequency, and the connections to the set for speed and voltage control are as follows:—

Both the motor and alternator fields, each having high resistances, were controlled by high resistance (2,800 ohms), potential dividers of the Isenthal type placed directly across the 200 volt

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main. A starting resistance of about 260 ohms was introduced into the motor armature circuit, and by joining P and Q speeds could be obtained from zero to the normal speed of the machine (2,000) by sliding the contact, thus using the starting resistance as a potential divider. Further increase of speed is obtained by weakening the motor field. The alternator field is controlled from zero to a maximum by its own potential divider.

The Vibration Galvanometer.

As a means of detecting potential differences on the bridges, etc., used, a Duddell vibration galvanometer was employed. As this instrument proved rather insensitive at the higher frequencies, a considerable amount of research work was done with a view to improving the instrument, and the results of this research are published in the *Proceedings of the Physical Society of London* under the headings, " The Maximum Sensibility of a Duddell Vibration Galvanometer," Vol. XXIV, Part IV, June 15th, 1912, and " Vibration Galvanometer Design," Vol. XXV, Part IV, June 15th, 1913. The improvements brought about in the instruments are briefly as follows:—

(1) Use of short pole pieces, so that with short wires at high frequencies all the flux can still be sent through to moving system.

(2) Use of electromagnet so that flux can be varied to obtain the maximum sensibility, the condition being that the back E.M.F. of the moving system be made equal to and in phase with its I R drop.

(3) The short-circuiting or cutting out of the inoperative part of the wire as the bridge pieces are brought together, thus reducing the effective resistance of the instrument, and allowing greater flux densities to be used. With these improvements carried out, the vibration galvanometer is a very satisfactory instrument for bridge work. The sensibility of this improved type is much greater than that of any other present type of vibration galvanometer.

The Thermostat.

Means for keeping the temperature constant within limits were required, so the following electrically operated thermostat was evolved which, without any special precautions, will keep the temperature constant within $\pm \frac{1}{1000}$ °C. This figure was obtained from the cooling curve of the tank and from the average times during which the heating was on and off. The instrument works with a definite period, depending on the difference of the tank and air temperatures.

The thermostat proper consists of a very thin glass bulb filled with toluene, and having a connecting limb containing mercury attached. The mercury arm is constricted at its upper part for about one inch, and the amount of mercury is so adjusted that at the temperature at which it is required to work the thermostat the end of the mercury column is inside the capillary. Electrical contact is made with the mercury below the capillary by means of a platinum wire fused through the glass, and there is an upper contact consisting of a very fine platinum wire which can be moved up or down the

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capillary in order to obtain an exact temperature adjustment. These two contacts are connected through a Leclanché cell and a large resistance to a polarised telegraph relay. The bias of this relay is so adjusted that the magnets of the heating lamp relay are normally short-circuited. This relay is excited by the current taken by the stirring motor. When the thermostat mercury makes contact with the platinum wire at S the polarised relay is excited and swings over to the stop Q, breaking the short-circuit of the lamp relay at P. The armature of the lamp relay is then attracted, thus cutting off

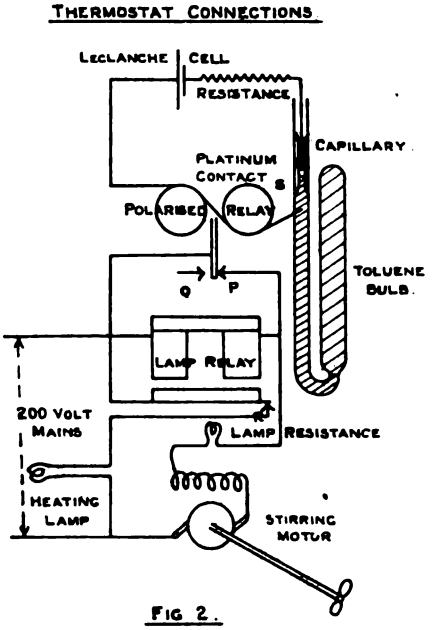

FIG 2.

the heating lamp. On a slight cooling taking place, the contact S is broken, and the contact P is again made, short-circuiting the lamp relay and switching on the heating current again. To damp out any vibrations of the mercury surface at S, the space above S is filled with B.P. paraffin. As the current passing S is very small, being of the order of a milliampere or two, the contact at S keeps perfectly clean, and very definite and sure working is obtained.

This thermostat has now run without any trouble and with practically no adjustment for several years.

The Conductivity Cells.

A number of cells were constructed with platinum and Jena glass, and, after a number of preliminary experiments, a couple of cells were used having platinum electrodes each 5×2 cms., separated 1 cm. The electrodes were not platinised, and a number of experiments were made with the electrodes in this state. Afterwards the electrodes of one cell were platinised and comparison tests were made with the platinised and non-platinised cells.

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Bridge Arrangements.

As a general rule, either one or other of the following arrangements was used.

The cell is denoted by a resistance R in series with a condenser C. In series with it is placed a variable self-induction L_1, and in the adjacent arm of the bridge another self-induction is introduced in order to balance the minimum self-induction of the variable one when the electrolytic cell is short-circuited. The bridge was usually an even ratio, one balance being obtained initially with the cell short-circuited. The cell is then introduced, and the bridge is again balanced by the introduction of self-induction into the cell arm and resistance R into the adjacent arm. Then the *cell* resist-

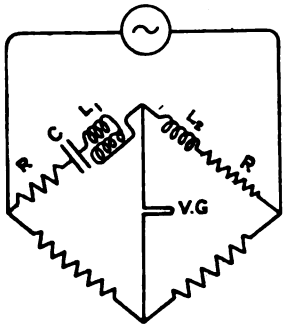

FIG. 3.

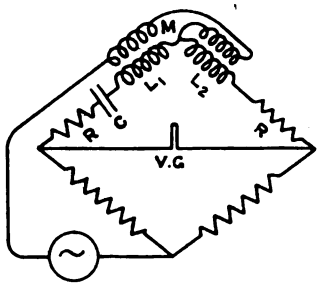

FIG. 4.

BRIDGE ARRANGEMENTS.

ance is R, and its capacity C is

$$C = \frac{1}{(L_1 - L_2)\, w^2} \text{ where } w = 2\pi f., \text{ and } L_1 - L_2$$

is the difference between the initial and final self-inductions. For L_1 an Ayrton-Perry variable standard of inductance was used.

Similar results may be obtained by using a Campbell standard of mutual induction, and this is a rather more convenient piece of apparatus to use, as it permits a zero setting of the bridge without the use of any other inductance.

If M_0 is the mutual inductance required to balance the bridge with the cell out, and M is the mutual inductance and R the additional resistance required with the cell in the bridge,

Then cell resistance = R and

$$\text{Cell capacity} = \frac{2}{(M - M_0)\, w^2}$$

In both these cases the alteration of R and L or M must proceed simultaneously, as no balance can be obtained until both equations are satisfied. In the following measurements the capacity of the two electrodes in series is given, the capacity tf either being double this value.

The above only holds true provided the capacity is a constant quantity during the current cycle. If the capacity varies the current

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wave will be distorted and absolute balance will be impossible. The experiments have shown that an absolute balance is always possible, therefore we may treat this capacity as being a constant quantity as far as one particular set of electrical conditions is concerned. After some preliminary experiments with various electrolytic cells experiments were carried out with two similar cells, having electrodes 5 × 2 cm. placed 1 cm. apart. Both cells had unplatinised electrodes at the start, and a number of experiments were carried out to find the resistance and capacity relationship between the cells before platinising one of them.

Cell No. 1 was filled with a decinormal solution of KCl, and the first experiment was to find what alteration—if any—was brought about in the resistance measurement by altering the current through the cell.

The following were the results obtained:—

TABLE 1.

R.	Current milliamps.
8.60	0.50
8.60	1.51
8.60	3.00
8.60	4.03
8.59	4.86
8.59	7.85
8.58	11.62
8.57	16.52
8.55	21.25

$\frac{KCl}{10}$ Pot No. 1. temp.: const.: 18° C., f const. = 182. The capacity effect was practically constant at 117 mfds. It seems fairly safe to use a current of 7 or 8 milliamperes through the cell. A current of about 4 milliamperes was used in the experiments following. The resistance frequency curves for the two pots were then taken between the limits of frequency 100 and 260.

The average results obtained were as follows:—

TABLE 2.

f	R cell 1.	R cell 2.
100	9.64	9.88
120	9.32	9.56
140	9.04	9.26
160	8.82	9.02
180	8.62	8.82
200	8.44	8.62
220	8.28	8.45
240	8.16	8.31
260	8.06	8.18

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Solution $\frac{KCl}{10}$ Temp. 18° C., current const. = 4 milliamps. The average capacity values obtained were:—C_1 = 117.3 mfds.; C_2 = 120.4 mfds., and the resistances varied with the frequency according to the following equations:—

$$R_1 = 22.91\, f^{-0.188}, \quad R_2 = 24.59\, f^{-0.198}$$

After these readings had been taken the temperature at which the cells were kept was changed to 25° and all future experiments, unless otherwise stated, are done at that temperature. At 25° the resistance frequency equations were: $R_1 = 21.98\, f^{-0.206}$. $R_2 = 22.24\, f^{-0.20}$ A few dilution experiments were carried out on No. 2 cell, but in view of the long series of dilution experiments given further on, only the equations of resistance and frequency are given.

TABLE 3.

No. 2 Cell 25° C.

$\frac{1}{10}$ KCl	$R = 22.24\, f^{-0.20}$
$\frac{1}{20}$ KCl	$R = 29.89\, f^{-0.154}$
$\frac{1}{40}$ KCl	$R = 42.96\, f^{-0.109}$

The diminishing effect of frequency variation on resistance will be noticed.

The electrodes of cell No. 1 were now platinised, using a 3 per cent. solution of H_2PtCl_6 containing $\frac{1}{40}$ per cent. of lead acetate (Kohlrausch).

Each plate had about 3 hours each at 0.05 amp., and 6 hours each at 0.1 ampere.

Using a decinormal solution of KCl, the following results were obtained:—

The total variation in resistance as the frequency was altered from 120 to 1,000 (the 1,000 frequency alternator was built at this time) was from 5.684 to 5.649 ohms, namely, 0.035 ohm, equivalent to a decrease of 0.615 per cent. This gave for the resistance capacity of the pot at $1{,}000 f \frac{\text{electrode area}}{\text{mean distance apart}} = 0.0724_4$, the conductivity of the $\frac{KCl}{10}$ being 0.01288.

Previously the resistance of this cell at 25° C. and 100 frequency was 8.52 ohms, and it diminished to 6.90 ohms at 258 frequency, an alteraton of 19 per cent. It is to be regretted that the 1,000 f alternator was built after these preliminary tests, but referring to a later table, it will be seen that the apparent resistance of $\frac{1}{10}$ KCl diminishes 30 per cent. when frequency is raised from 100 to 1,000, using cell 2 with non-platinised electrodes.

The capacity of the cell has been changed from about 120 mfds. at 120 f to 21,900 mfds., an increase of 183 times.

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A series of dilution tests was carried out, using both the platinised and unplatinised electrodes. The starting solution was $\frac{1}{10}$ KCl, and measurements were made at various frequencies between 100 and 1,000, the apparent resistance and capacity of the cell being measured. The solution was then diluted to approximately half strength, and the readings were repeated. The dilution process was carried out eight times, and the results are summarised in the following tables:—

TABLE 4.

Cell with Platinised Electrodes.

Solution Approximate Strength.	Resistance at 1000 *f*.	Resistance at 100 *f*.	$\frac{R_{100}}{R_{1000}}$	% Incr. in Resistance.	Capacity at 1000 frequency	Capacity at 100 frequency	Capacity Frequency Equation farads.	Conductivity.
$\frac{1}{10}$ KCl	5.624	5.676	0.502	0.925	4200	27000	$C=0.871f^{-0.765}$	01288
$\frac{1}{20}$	11.043	11.122	0.089	0.806	3620	16550	$C=0.3366f^{-0.656}$	00656
$\frac{1}{40}$	22.242	22.239	0.148	0.665	2260	10600	$C=0.379f^{-0.738}$	00325
$\frac{1}{80}$	43.489	43.733	0.244	0.564	1622	6810		001665
$\frac{1}{160}$	84.838	85.258	0.420	0.495	1072	4540		000853
$\frac{1}{320}$	163.150	164.085	0.935	0.572	1072	3040		000444
$\frac{1}{640}$	315.40	318.10	2.70	0.857	633	1760		000229
$\frac{1}{1280}$	564.0	570.72	6.72	1.19	108	1282		000128
$\frac{1}{2560}$	1107.0	1124.2	17.2	1.71	30.2	698		0000654
Cell with Unplatinised Electrodes.							mfds.	
$\frac{1}{10}$	6.329	9.013	2.684	42.5	81	120	$C=248f^{-0.165}$	01288
$\frac{1}{20}$	11.950	15.115	3.165	26.5	85	121	$C=223f^{-0.14}$	00656
$\frac{1}{40}$	23.666	27.320	3.654	15.4	69.6	106		00325
$\frac{1}{80}$	45.710	49.55	3.84	8.4	68.5	98		001665
$\frac{1}{160}$	89.20	93.25	4.05	4.5	59.0	103		000853
$\frac{1}{320}$	169.60	175.00	5.40	3.2	54.7	77		000444
$\frac{1}{640}$	334.70	343.08	8.38	2.5	59.8	79		000229
$\frac{1}{1280}$	585.00	599.43	14.43	2.5	36.1	68		000128
$\frac{1}{2560}$	1137.4	1146.8	9.4	0.8	17.6	65		0000654
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)

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These dilution experiments give some extremely interesting results.

It will be noticed that even using platinised electrodes, the resistance of the cell varies with the frequency, although for strong solutions this variation is small compared with the variation which takes place in the cell having non-platinised electrodes.

As dilution proceeds, the percentage resistance variation decreases up to a point, and then it commences to increase until with dilute solutions the resistance variation with frequency is just as bad with the cell having platinised electrodes as with the cell having non-platinised electrodes. The resistance variations of the non-platinised cell are very large with strong solutions, a 42.5 per cent. variation being noticed with the decinormal KCl—but this variation diminishes rapidly as the dilution proceeds, although the rate of resistance alteration is not inversely proportional to the dilution as might at first be supposed. It would appear, then, that with dilute solutions it is preferable to use non-platinised electrodes, because the percentage resistance variation with frequency is of the same order as obtained with the platinised electrodes, but whereas the variation is increasing with the platinised electrodes, it is decreasing when the non-platinised electrodes are used, and furthermore the use of non-platinised electrodes is preferable, as many experimenters have found that platinised electrodes alter the strength of the solution due to an absorption of salt molecules by the platinised surface.

It will be noticed in every case that dilution means a decrease in the effective capacity of the cell.

In order to see how R was altering as the angle of lead of the current altered the angles $\theta = \tan^{-1} \frac{1}{\omega CR}$, where C and R are the equivalent capacity and resistance of the cell, were calculated for various values of the frequency. A line OA was drawn making an angle θ with the X axis; the value of the resistance OB was then marked off on the X axis, and an ordinate BA was drawn cutting the vector OA at A. Then OA is the impedance of the cell, AB is its reactance, and BO is the equivalent resistance of the cell. On drawing these points in for $\frac{KCl}{10}$ it was found that the locus of these points was a straight line, and, as this line cuts the X axis at a point of infinite frequency, this should give the true resistance of the electrolyte. The point found corresponded very closely with that calculated from the resistance of the platinised cell using the same solution. (The ratio between the cells was determined before platinisation.) From this locus we obtain the following equation for the true resistance of the electrolyte. $R = R_1 - \frac{\tan \alpha}{2 \pi f C}$ where α is the angle made by the locus and the axis of X. This process was repeated for the number of the KCl solutions, with the same result each time, and it is interesting to note that as dilution proceeds tan α is approximately a constant quantity. The equations connecting C and f have been worked out in several cases, and the following are the resistance equations obtained by putting in these values

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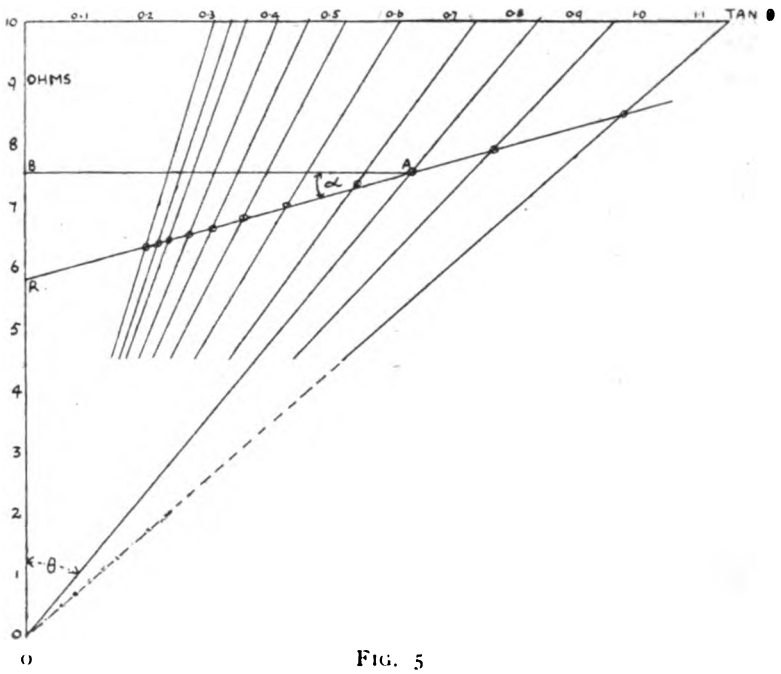

FIG. 5

TABLE 5.

KCl/10 Non-Platinised Cell.

Frequency.	Resistance.	$\tan\theta = \frac{1}{wCR}$
150	8.445	1.150
200	7.921	0.965
250	7.564	0.836
300	7.357	0.738
400	7.013	0.610
500	6.786	0.522
600	6.643	0.460
700	6.537	0.412
~~800 9100~~	6.436	0.362
~~900 800~~	6.376	0.338
1000	6.329	0.310
Infinity	5.790	0.000

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TABLE 6.

Solution KCl	tan α	Eqn. for C and f	Resistance and f
		μf	
$\frac{1}{10}$	0.295	$C = 248.4\, f^{-0.165}$	$R = Rf - 177.7\, f^{-0.835}$
$\frac{1}{20}$	0.295	$C = 223.4\, f^{-0.14}$	$R = Rf - 250 f^{-0.86}$
$\frac{1}{40}$	0 295	$C = 182.9\, f^{-0.137}$	$R = Rf - 238 f^{-0.863}$
$\frac{1}{80}$	0.295		
$\frac{1}{160}$	0.295		

In Fig. 5, tan α is the ratio of the apparent resistance of the the condenser to its reactance, and is constant, *i.e.*,

$$\tan \alpha = Rw C = \text{constant.}$$

Decinormal solutions of potassium, sodium, ammonium, iron, nickel, and cobalt were experimented with, and the polar locus of the impedance with respect to the current was always a straight line.

The resistance of the electrolyte at infinite frequency can be calculated as follows:—

If R_1, C_1, R_2, C_2 are the apparent resistances and capacities at frequencies f_1 and f_2,

$$R_{w=\infty} = R_1 - \frac{\tan \alpha}{w_1 c_1}$$

$$= R_1 - \frac{R_2 - R_1}{\left(\frac{1}{w_2 c_2} - \frac{1}{w_1 c_1}\right) w_1 c_1}$$

$$= \frac{R_1 w_1 C_1 - R_2 w_2 C_2}{w_1 c_1 - w_2 c_2}$$

From this expression, knowing the constant of the cell, the true conductivity of the solution can be found.

The resistance of the electrolyte as extrapolated from the polar locus agrees very well with the calculated locus except in the case of NH_4Cl, which results require repeating. The very much greater capacity and greater variation of capacity with frequency in the case of the platinised cell will be noticed.

It does not appear to me to be reasonable to attribute the large increase of capacity noticed on platinising the electrodes entirely to an increase of area; it seems to me to be much more likely that platinising the electrodes has brought them into closer contact with the electrolyte. Spongy platinum—if one may term the deposited platinum spongy—has a peculiar effect on gases, and it may be that the normal gas film is to a large extent absorbed by the platinum black, thus enormously increasing the capacity of the electrodes to the electrolyte, reducing the voltage across this dielectric per unit current, and

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TABLE 7.

The following results were obtained :—

Solution Decinormal	Cell.	Resistance. $f = 200$	Resistance. $f = 1000$	Resistance Decrease.	% Decrease of R.	Capacity. $f = 200$ micro-farads.	Capacity. $f = 1000$ micro-farads.	Capacity. Decrease.	% Capacity Decrease.	Resistance calculated from locus curve.	Resistance calculated from platinised cell readings.	$\tan \alpha = R\omega C$
KCl	Non-Plat.	7.921	6.329	1.592	20.1	104	81	23	22.1	5.75	5.72	0.295
	Platinised	5.656	5.624	0.032	0.56	15800	4220	11580	73	—	—	—
NaCl	Non-Plat.	8.70	7.35	1.35	15.6	117	88	29	24.8	6.83	6.76	0.276
	Platinised	6.70	6.58	0.12	1.8	12000	5870	6130	51	—	—	—
NH_4Cl	Non-Plat.	9.35	7.78	1.57	16.8	127	94	33	26.0	7.22	5.32 (?)	0.332
	Platinised	5.273	5.245	0.028	0.53	14000	8800	5200	37	—	—	—
$FeCl_3$	Non-Plat.	4.07	3.40	0.67	16.5	206	158	48	23.3	3.16	3.07	0.236
	Platinised	3.06	3.03	0.03	0.98	—	—	—	—	—	—	—
$NiCl_2$	Non-Plat.	5.40	4.44	0.96	17.8	167	129	38	22.6	4.13	4.08	0.262
	Platinised	4.062	4.004	0.058	1.43	13700	—	—	—	—	—	—
CoCl	Non-Plat.	5.35	4.28	1.07	20.0	157	119	38	24.1	3.89	3.86	0.293
	Platinised	3.840	3.795	0.045	1.17	14000	8450	5550	40	—	—	—

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reducing the losses. The ratios of the capacities of the platinised to the unplatinised plates are given in Table 8 for various degrees of dilution. The ratios are given for frequencies 1,000 and 100, and it will be noticed that this ratio is not a constant quantity, it varies not only with frequency, but with dilution, an increase of frequency having the same effect as dilution, namely, an increase of

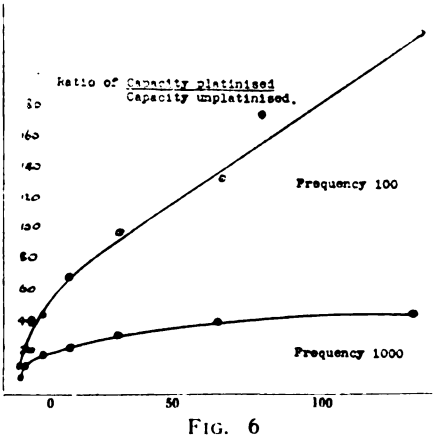

FIG. 6

TABLE 8.

Conductivity (10^{-4})	Capacity platinised / Capacity unplatinised Frequency.	
	100	1,000
128.8	233	51.7
65.6	137	42.5
32.5	100	32.4
16 6	69.5	23.7
8.53	44.0	18.2
4.44	39.5	19.6
2.29	22.2	10.6
1.28	18.9	3.0
0 654	10 7	1.7

the apparent film thickness; the assumption that platinisation simply increases the electrode area would necessitate the ratio of the platinised area to the unplatinised area remaining a constant. The fact that the ratio alters so enormously and that at high frequencies and dilution there is very little to choose between an unplatinised or platinised electrode seems to indicate that some other explanation is necessary.

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The effect of temperature alteration on a decinormal solution of KCl at two different frequencies was tried. The results were as follows:—

TABLE 9.

Non-Platinised Cell.

Temp.° C.	Resistance.	Capacity. mfds.	Frequency.	Tan. $\theta = \frac{1}{wCR}$.
25.0	5.9	85	940	0.317
29.9	5.5	90	940	0.346
34.5	5.1	88	940	0.355
40.2	4.7	81	940	0.415
25.0	7.21	122	200	0.181
29.9	6.75	123	200	0.192
34.4	6.45	127	200	0.194
40.5	6.00	135	200	0.196

In the case of the non-platinised cell the two resistance temperature curves are parallel straight lines, giving the same temperature coefficient at the two frequencies, and it will be seen from the figures that the capacity effect varies only very slightly with the temperature.

The resistance temperature equations are as follows:—

$$R_{200f} = 9.25 - 0.0813\,t$$
$$R_{940f} = 7.95 - 0.0813\,t$$

An increase of frequency of from 200 to 940 is equivalent to a fall of temperature of 36° C. It is interesting to note that from the resistance equation at 940 frequency the KCl would have no resistance at 97.5° C., *i.e.*, near the boiling point of water. These higher temperatures have not been experimented with as yet.

The platinised cell gave very much the same results, except that the two lines were very close together. The resistance equation being $R_t = 7.25 - 0.078t$. The capacity was very large, and its variations were inappreciable on the bridge.

Some of these cell resistance variation experiments were shown at a meeting of the Physical Society of London in 1911 (*Phys. Society Bulletin*, March, 1911), and it was suggested by the author then that the resistance of an electrolyte might vary with frequency. Smith and Moss made some experiments on this point. (The Resistance of Electrolytes, by S. W. J. Smith, M.A., D.Sc., and H. Moss, B.Sc., *Proc. Phys. Soc.*, Jan. 24th, 1913). The resistance of an electrolyte normal KCl was determined by the "simultaneous measurement of the voltage between the ends of a tube containing the electrolyte and of the current passing through it. The former were measured by means of an Ayrton-Mather electrostatic voltmeter connected to auxiliary electrodes, and the latter by means of a Duddell thermo-galvanometer. In the cases examined it was found that the resistivity of the electrolyte was constant within 0.05 per cent., whether steady currents of any frequency or currents of any frequency up to 2,300 alternations per second were used."

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These experiments, although conclusive as far as they go, do not give a very easy method of determining electrolytic resistance. The method is indirect, depending on the calibration of an electrostatic voltmeter and a thermo-galvanometer, both being instruments requiring a considerable amount of skilled handling to give satisfactory results. A method giving a direct check against a known resistance is, I think, preferable, especially when some null method of checking can be employed. To be able to measure a large number of very different resistances would require either a large selection of instruments or a great variety of sizes of electrolytic cells.

The experiments of Smith and Moss suggested to the author that the Drysdale potentiometer might be satisfactorily used to make a series of tests using potential electrodes. The Drysdale potentiometer consists of an ordinary potentiometer in conjunction with an ammeter and a phase shifting transformer. The phase shifting transformer consists of a stator and rotor—which can be turned relatively to the stator by means of a worm and wheel—similar to an induction motor. The stator winding is two-phase, producing a rotating magnetic field which induces an E.M.F. in the rotor, whose phase relationship relative to the main supply can be altered by simply turning the rotor through any desired angle. The potentiometer is fed from the rotor, and the current is kept constant. The instrument is then used like an ordinary potentiometer, except that a vibration galvanometer is employed, and voltages must be balanced for direction as well as magnitude. The operation demands a double measurement, firstly, the measurement of the voltage across the potential electrodes in terms of the potentiometer resistances, and, secondly, a measurement of the voltage across a standard resistance in series with the cell; the ratio of these two voltages multiplied by the standwar resistance giving the resistance between the potential electrodes.

One of the bad points about the design of the instrument is the large proportion of the rotor voltage absorbed by the milli-ammeter, namely, six out of eight volts. This means that for low frequencies at least 50 volts are required on the stator of the phase shifter, and more as the frequency increases. Where small special machines, such as those used in the present research, are employed, this is a great disadvantage, and in the present case the ammeter was short-circuited and a reflecting dynamometer, only taking a very small voltage, was used with very satisfactory results.

Some tests on KCl are given in Table 10, and it will be seen that the resistance between the point electrodes was practically constant, while that between the current electrodes varied.

There seems to be a phase displacement of about $\frac{1}{2}°$ between the voltage across the non-inductive anti-capacity resistance and the potential electrodes. This was probably due to the resistance.

Owing to the considerable amount of manipulation required in working the Drysdale potentiometer, *e.g.*, the speed must be kept quite constant or an elliptical rotating field instead of a circular field is produced—the following potentiometer arrangement was evolved by the author, which has the advantages of cheapness and simplicity, as it can be made out of apparatus which is at the disposal of most physicists (Fig. 7).

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It consists essentially of an electrolytic cell PQ in series with a shunted condenser C and a potentiometer RS. The potentiometer may be a Crompton potentiometer, as this has been found suitable up to 250 frequency. If RS is an ordinary potentiometer, a standard resistance HK may be introduced for purpose of calibrating it. Across the alternator terminals is connected an air core transformer T, having a variable coupling, which may be produced by turning the coils relatively to one another, moving them farther apart or by both processes. They may consist of simply a couple of coils of wire moving along a stick, or an Ayrton-Perry variable self-induc-

TABLE 10.

Frequency.	Potentiometer reading across Standard resistance of 300 ohms		Potentiometer reading across potential electrodes		Resistance between potential electrodes	Potentiometer reading across electrodes		Resistance between electrodes
	V	θ°	V	θ°	R	V	θ°	
Solution $\frac{KCl}{10}$								
188	11834	+2	12932	$+1\frac{1}{2}$	327.9	16897	1°	428.4
188	11836	+2	12914	$+1\frac{1}{4}$	327.3	16900	1	428.4
188	11818	+2	12907	$1\frac{1}{2}$	327.66	16863	1	428.1
415	11555	8+	12647	$8\frac{1}{2}$	328.35	16390	$8\frac{1}{2}$	425.5
415	11595	+9	12670	$8\frac{1}{4}$	327.81	16425	$8\frac{1}{2}$	425.0
880	1180	+16	1290	15	327.96	1660	15	422.0
Concentrated Solution KCl.								
	Stand. Resist. 10 ohms.							
997	1005	10.5	9660	10	0.961	1302	8	1.295
997	1002	10.7	9650	10	0.963	1302	8	1.299
182	8703	+1	8378	$+\frac{1}{2}$	0.963	1203	−5.7	1.382
182	8695	+1	8400	$+\frac{1}{2}$	0.966	1204	−5.5	1.385

tion may be used by disconnecting the fixed coil from the moving coil, or, better still, a Campbell variable standard of mutual induction will be found very convenient. In the absence of any of these variable inductances or mutual inductances, a perfectly satisfactory arrangement can be easily made, as the value of the coupling is not required to be known. On account of the IR drop in the primary of the air transformer, the secondary E.M.F. is leading on the primary applied voltage by a small angle. The use of the shunted condenser is to give the potentiometer current the same angle of lead as the secondary voltage. The method of operation is as follows:—

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The secondary AB is connected through the vibration galvanometer VG to the potential electrodes PQ. The distance apart of the coils of the transformer is adjusted and the resistance shunting the condenser is adjusted until there is no deflection of the vibration galvanometer. The voltage across AB is then equal to *and in phase* with the voltage across PQ. The secondary of the transformer AB is now connected to the points R and S, and the contacts R and S are moved until there is no deflection. Then the resistance between PQ is equal to the resistance between RS. The potentiometer may be calibrated in resistance by the same process by checking against a standard resistance HK. This method is very quick and simple in operation, and gives a check directly against a standard resistance by a null method.

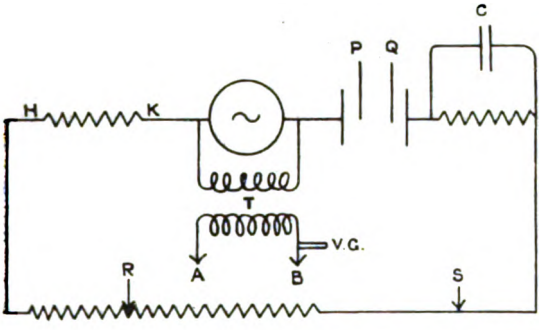

FIG. 7.

A number of experiments performed by this method proved fairly successful. The manipulation was easy, but there seemed to be a small phase displacement between the voltage across the potential electrodes and that across the standard resistance which necessitated a small alteration of the shunt across the condenser to obtain absolute balance. This phase displacement was mentioned previously when working with the Drysdale potentiometer, but was put down to the standard resistance. In order to make sure as to the cause of this phase displacement a further series of experiments was carried out, using the Drysdale potentiometer. As the angles concerned with were small—of the order of $\frac{1}{2}°$ or so—and as the phase shifter scale was only marked in degrees, the circular head of the phase shifter worm was divided into degrees and tenths of a degree, and could easily be read to 0.01°. In order to keep the worm wheel of the phase shifter always in contact with the worm, a spiral clock spring was fitted, which kept the worm wheel and worm always pressed against one another in the same direction. This arrangement proved very satisfactory, and measurements of phase displacement could be made to 0.01° *and repeated*.

In the first set of experiments a U tube was used carrying a set of current and a set of potential electrodes. The electrodes were of plain platinum, and the potential electrodes were set in front of the current electrodes, *i.e.*, they were in the main current stream.

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The following results were obtained:—

TABLE 11.

Resistance.	Angle of lag of voltage on current.	Frequency.	Remarks.
15.352	1.70	232	Solution saturated KCl.
14.868	2.63	640	Current and potential electrodes plain platinum.
14.519	2.76	980	Potential electrodes in current stream.

A Paul decade box, anti-capacity and non-inductive, was used as the standard resistance, and an experiment was made here to see if there was any phase displacement between the voltage across 10 one-ohm coils and one ten-ohm coil. No phase displacement was found, so it looked as if the phase displacements observed in the experiment were due to the potential electrodes or to part of the current being transmitted as a capacity current.

The effect of using mercury electrodes was then tried. The most convenient vessels at hand were some H tubes such as are used in the manufacture of standard cadmium cells. Mercury was introduced into the two bottom limbs of the H and plain platinum electrodes were used as the current electrodes.

A saturated solution of KCl was used, and the following results were obtained:—

TABLE 12.

R.	Angle of lag of voltage on current.	Frequency.	Remarks.
8.26	0.26	216	Potential electrodes Mercury.
8.28	0.16	235	Solution saturated KCl.
8.26	0.33	537	
8.26	0.59	980	

It will be noticed that the impedance is now practically a constant quantity, as the frequency varies, and that the phase displacement is very much smaller than before. At the time this was put down as a virtue of the mercury electrodes, but later experiments have shown that this is not so.

Experiments were now made with two H tubes having mercury current electrodes at the bottom and platinum potential electrodes at the top; one set of electrodes was platinised, and and the other set was plain. A saturated solution of KCl was put in the cells, and experiments were made to see if there was any difference of action between the non-platinised and the platinised

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potential electrodes. The potential electrodes extended to the horizontal arm of the H, and so were partly in the main current stream. Owing to the peculiarity of the results obtained, a set of experiments was made with the potential electrodes at the top parts of the H, *i.e.*, as far out of the current stream as possible.

The following were the results obtained:—

TABLE 13.

Frequency.	Non-Platinised Potential Electrodes.		Platinised Potential Electrodes.		Remarks.
	Resistance.	Phase displacement of voltage lead °	Resistance.	Phase displacement of voltage lag °	
216	10.74	+0.19	9.84	−0.25	Saturated solution of KCl used.
490	10.77	+0.23	9.79	−0.24	Potential electrodes in current stream.
1000	10.81	+0.28	9.77	−0.17	
*216	10.75	+0.19	9.84	−0.26	*Check reading 1½ hours from first reading.
		lag		lag	
210	9.82	−0.01	8.59	0	Potential electrodes as far out of main current stream as possible.
500	9.82	−0.04	8.59	−0.04	
980	9.82	−0.04	8.59	−0.07	

The results are rather curious; with the non-platinised electrodes in current stream we have a slight increase of resistance with frequency, and the current is lagging very slightly on the voltage; with platinised electrodes the resistance decreases very slightly with the increase of frequency, the current leading the voltage by a fraction of a degree. Previous experiments (Table 11) with the same solution and plain electrodes, gave a decreasing resistance with increase of frequency, the current leading the voltage by a small angle. The variations with the U tube were much greater than those with the H tube, so I tried the effect of removing the potential electrodes as far out of the current stream as possible, in other words they were put in an electrical backwater. The results shown in the previous table were very satisfactory, the impedance remaining constant, and the phase displacement between the voltage across the potential electrodes and the voltage across the standard resistance used being very small.

It would appear from these experiments that in working with very strong solutions with low resistance cells using potential electrodes that very satisfactory results can be obtained by keeping the potential electrodes as far out of the main current stream as possible.

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Some experiments were then tried, using a modification of the potentiometer arrangement shown in Fig. 7, where the E.M.F. across the secondary of an air core transformer having a variable coupling is made equal to and in phase with the voltage across the potential electrodes of the cell. If instead of exactly counter-balancing this voltage by the voltage across the part of the potentiometer RS, we have the variable air core transformer calibrated in terms of mutual induction of the two coils and note the reading M_1 when the secondary is across the potential electrodes of the cell, and then connect the secondary across a standard resistance HK, noting the mutual induction M_2 required to again balance, then the resistance X between the potential electrodes of the electrolytic cell is equal to

$$X = \frac{M_1 R}{M_2}$$

where R is the standard resistance used. This method has been tried for various frequencies, and has proved very easy to manipulate, and has given the same results for frequencies up to 1,000.

The following are some of the results obtained with one of the H cells previously used:—

TABLE 14.

Frequency.	Potential electrodes of cell M_1 microhys.	Standard Resistance 10 ohms. M_2 microhys.	Resistance between Potential electrodes.	Remarks.
250	939	957	9.81	Campbell variable standard of Mutual Induction used.
	937	955	9.81	
	935	954	9.81	
495	86.7	88.3	9.82	Condenser in circuit varied from 6 mfds. to .6 mfds. with a shunt of 70 ohms.
	86.7	88.3		
655	845	862	9.81	Solution saturated KCl.
	845	862		
1000	888	906	9.80	
	888	906		

Conclusions.

A brief summary of some of the conclusions arrived at during the research are here given:—

In measuring the resistance of an electrolyte in a bridge we have, in addition to the electrolytic resistance proper, to deal with the resistance and capacity of a gas film which interposes between the electrodes and the electrolyte. This gas film behaves like a leaky condenser, and its thickness and resistance depend on the strength of the solution employed and on the temperature, current flowing through the cell, and the frequency of the supply. An increase of temperature acts like an increase of current, the gas film thickness diminishes in each case. With increase of frequency the film appar-

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ently becomes thicker, as the apparent capacity of the electrodes diminishes. Although this film apparently becomes thicker with increase of frequency, its losses apparently decrease, because increase of frequency is always followed by a decrease in the apparent resistance of the cell. If the impedance of the cell be plotted in correct phase relationship to the current through it for a number of different frequencies, the locus of the impedance is a straight line, which cuts the current axis at the point of infinite frequency, and the intercept on the current axis is the true resistance of the electrolyte.

The effect of platinising an electrode is not simply to increase its area, in my opinion any increase of area has very little to do with the differences caused by platinisation. If the effect produced were one of increased area the ratio of the capacity effects of the platinised cell to the unplatinised cell would remain constant for different frequences and strength of solutions; but it most decidedly does not. The percentage resistance variation with dilution diminishes to a certain point, and, as dilution proceeds, begins to increase again, with platinised electrodes, whereas with non-platinised electrodes the per cent. resistance variation always diminishes as dilution proceeds, and with dilute solutions the non-platinised electrode is electrically equally as suitable as the platinised electrode, while chemically it is superior, as there is no absorption of salt, etc., as with the platinised electrode.

It seems to me that the effect of platinising the electrodes is to produce a deposit of spongy platinum which is capable of more or less absorbing the gas film; in other words, we can imagine the gas film to be more or less short-circuited by tentacles of platinum extending from the platinum surface towards the electrolyte; then the enormous increase of capacity observed on platinising is not due to increased area of electrodes, but to diminished thickness of the gas film. The result of the impedance locus with respect to current of an electrolytic cell being a straight line, is that the condenser formed by the gas film varies in the following manner with frequency $R \times C = \frac{1}{f}$ where R is the equivalent resistance of the film, *i.e.*, it is the resistance which would have to be put in series with the capacity C in order to produce the same losses as those which occur in the film.

Experiments by Smith and Moss, using high resistance cells and a voltmeter-ammeter method have shown constancy of impedance over a wide range of frequency.

The author's experiments, using strong solutions and low resistance cells, have shown by various potentiometer methods that the resistance of an electrolyte is independent of the frequency within the limits of frequency used, but that in order to obtain this result the potential electrodes should be put into an electrical backwater, *i.e.*, out of the main current stream.

Finally, accurate measurements of resistance by bridge methods can be made with cells having either platinised or non-platinised electrodes using any strength of solution and resistance of cell, provided that balance is obtained by one or other of the methods described here, or any equivalent method, at two different frequencies

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and that the impedance be plotted with regard to its phase displacement to the current, then the impedance locus intercepts the current axis at the true resistance of the cell. In many cases using platinised electrodes the differences would be so small as to be negligible. Properly carried out ammeter voltmeter tests also give reliable results. Potentiometer results such as described also give correct results, but in all cases where accurate results are required the potential electrodes should be placed out of the main current stream. For simplicity and ease of working, I rather favour the potentiometer method which compares the voltages across the potential electrodes of the cell with the voltage across the standard resistance by means of a calibrated mutual induction. The method is quick, simple, and reliable.

I wish to express my thanks to Professor T. Mather, F.R.S., for his kindness in always enabling me to obtain the very best apparatus available and for his interest in the work, and also to Messrs. F. W. Andrews and J. T. Hedley, the workshop instructors at the City and Guilds Engineering College, for their skilled assistance in the manufacture of alternators, vibration galvanometers and the many things required in research work.

Discussion.

Dr. A. Fleck asked what was the frequency which was used. He had used a Crypto variable frequency alternator, and found that when working with currents of a frequency of 100, the resistance obtained did not coincide with the resistance obtained when using a frequency of 400. He had rather put it down as being due to decomposition products which were momentarily formed, and not being quite got rid of. The experiments, however, had not been continued.

Mr. W. R. Cooper asked the author what was the extent of the phase difference. He supposed an oscillograph could not be applied in this case because of interference with the measurement made. With regard to the double capacity of an electrolytic cell, that seemed rather a new idea, and he should think it was scarcely justified.

The Chairman said it was very much to be regretted that it was not possible to distribute copies of the paper before the meeting, because it was an important paper. Its subject had already been discussed very much by a class of people for whom he had the greatest respect, viz., chemists, but now it was being attacked by one who knew something about electrical engineering at the same time. For this reason new light might be thrown upon it, and he welcomed the paper very much. He agreed it ought to be discussed more, but if the discussion were to be postponed to another meeting, it meant postponing it until the autumn. He suggested, therefore, that they should discuss it as far as possible that evening, and leave it for those, who desired, to send in communications to the dis-

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cussion to be printed in the *Proceedings*. He hoped such communications would be sent in to the Secretary during the next month or so. His own doubts as to what to say about the paper at the present moment arose from a feeling of uncertainty as to what it was that was measured experimentally. He took it from what the author had said that he considered the quantity measured was the quantity R. He himself, without time to study the paper, was not at all sure that it was the resistance that was measured. Why was it not the impedance? Perhaps the author could remove that doubt. Taking the results as they stand, the implication is that

$$R - R_\infty = \frac{\tan \theta}{wC}$$

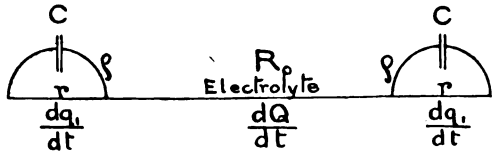
This equation asserts that the resistance measured is equal to the resistance of the corresponding infinite frequency, plus a term which is inversely as the capacity at the particular frequency and of the frequency itself. The consequence seems to be that the true resistance of the electrolyte is itself a variable quantity, depending on the frequency.

Mr. Haworth: No, I do not think so.

The Chairman said it varies down to the value R_∞, and if the resistance depends on the frequency, what was it they were measuring? It was that kind of question they wanted the opportunity of discussing more fully, and if the author could throw any light on it at the moment he would be very glad if he would do so.

(*Communicated later.*)

Perusal of the paper makes it quite clear that Mr. Haworth has measured the effective resistance and effective capacity of his cells. But when it comes to a question of interpretation of the results there is much room for discussion. The variation of these data with *current* is easy to understand; but it is not immediately obvious how the frequency produces a variation. Mr. Haworth attributes it to a variation of the thickness of the gas film upon the electrodes. This film he regards in accordance with established usage as a leaky condenser. He appears, however, not to have noticed that if the



film be so regarded, dependence of R and C upon frequency will arise even without any alteration in the film. A leaky condenser may be replaced by a capacity with a resistance in *parallel* with it. To obtain greater generality a resistance is also put in series with the capacity. The system equivalent to the cell would then be as in the accompanying diagram.

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The equations determining the current $\frac{dQ}{dt}$ through the body of the electrolyte are

$$R\frac{dQ}{dt} + 2r\frac{dq_1}{dt} = \text{alternating voltage} = V_0 e^{iwt}$$

$$r\frac{dq_1}{dt} = \frac{1}{C}(Q - q_1) + \rho\left(\frac{dQ}{dt} - \frac{dq_1}{dt}\right)$$

Solving these simultaneously we obtain, in the first place, the differential equation

$$\left[R + \frac{2r(\rho iw + \frac{1}{C})}{(r+\rho)iw + \frac{1}{C}}\right]\frac{dQ}{dt} = V_0 e^{iwt}$$

or, as it may be written:—

$$\left\{R + 2r\left[\frac{1 + \rho(r+\rho)C^2w^2 - iCrw}{1 + (r+\rho)^2C^2w^2}\right]\right\}\frac{dQ}{dt} = V_0 e^{iwt}$$

If we were dealing with a single capacity C_e and resistance R_e in series the equation would have been

$$\left(R_e - \frac{i}{C_e w}\right)\frac{dQ}{dt} = V_0 e^{iwt}$$

Comparing these equations, we see that the effective resistance is

$$R_e = R + \frac{2r[1 + \rho(r+\rho)C^2w^2]}{1 + (r+\rho)^2C^2w^2}$$

and the effective capacity is given by

$$\frac{1}{C_e} = \frac{1}{C}\,\frac{2r^2C^2w^2}{1 + (r+\rho)^2C^2w^2}$$

Both these effective values vary with the frequency, even though the detailed physical data are constants.

In order to compare with the experimental results write

$$y = R_e - R = \frac{2r(1 + K_1w^2)}{1 + K_2w^2}$$

which can be otherwise written

$$\left(y - 2r\frac{K_1}{K_2}\right)\left(1 + K_2w^2\right) = 2r\left(1 - \frac{K_1}{K_2}\right)$$

$$\text{or } (y-a)(w^2+b) = (2r-a)b.$$

Hence if y is plotted against w^2 the curve should be a rectangular hyperbola. The values for KCl/10 non-platinised (Table 5) when so plotted have, indeed, this character. I have calculated the values of the constants from these numbers,

$$a = 0.35. \qquad b = 4\pi^2 \times 640. \qquad (2r-a)b = 4\pi^2 \times 1990$$

and from these,

$$(r+\rho)^2C^2 = 1/4\pi^2(640)$$

$$\rho(r+\rho)C^2 = \frac{1}{9.9} \times \frac{1}{4\pi^2 \times 640}$$

whence r = 1.73 ohms, C = 3,000 mfds.

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Experimental and calculated values of $R_e - R$ are now tabulated:—

Frequency.	R_e Experimental.	R Calculated.
150 ...	2.655 ...	2.65
300 ...	1.567 ...	1.64
500 ...	.996 ...	.983
800 ...	.646 ...	.632
1,000 ...	.539 ...	.537

These values for $R - R$, which are, of course, only small differences of experimental numbers, fit a hyperbolic law very well. This correspondence justifies one in thinking that the variations arise in much the sort of way indicated in this note. The calculated value of C is, however, much in excess of the experimental one.

The above equations show that when the frequency is infinite

$$R_e - R = 2r$$

$$C_e = \frac{C}{2}\left(\frac{r+\rho}{r}\right)^2.$$

Mr. Haworth would, therefore, not be justified in taking the true resistance of the electrolyte, as being the values for infinite frequency: this would include the resistances of the two double layers on the electrodes. In the case worked out, the value of $2r$ is about 3.4 ohms. Until more is known in regard to the exact processes operating at the electrodes the interpretation of all investigations is unsafe.

I have written this note to show that caution is necessary in interpreting the results of these experiments. Mr. Haworth has made an important contribution by the scientific way in which he has balanced separately for resistance and capacity effects in an electrolytic cell. But the interpretations he makes are of very little value, and in some cases are certainly erroneous. In particular, the conclusion he draws in regard to the use of non-platinised electrodes seems to be exceedingly questionable. It is, in fact, only by working, as in Kohlrausch's method, under conditions in which the disturbance at the electrodes may be as small as possible (that is with high resistance cells and unpolarisible electrodes) that something like certainty is attainable.

Mr. G. L. Addenbrooke said he largely took the view of the author in thinking there were certain things which required further explanation in connection with electrolytic measurements. The author had experimented with electrolytes, but he himself had been working for many years on so-called insulating materials, and he was rather puzzled as to where the division came in, if there was one, between insulating materials and electrolytes.

He had never so far found out satisfactorily, in dealing with the poorer classes of insulators, whether the reactions extended downwards as the insulation got still poorer on the same lines, or whether some new factor came in when getting down to the resistances met with in electrolytes.

He had a strong impression that the results he had obtained with ordinary insulators were very similar to those described by the author with electrolytes, the differences being merely in the relative magnitudes of the actions and not in their fundamental character.

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He was clear that two forms of capacity had to be dealt with in insulating materials. The experiments he had made were chiefly on celluloid and other similar materials which held a certain proportion of moisture. These were dried and the capacity and resistance taken in a dried state both with steady and alternating currents. A small known weight of moisture was then allowed to be re-absorbed, and a fresh set of measurements made. This was repeated a number of times until the original amount of moisture was fully re-absorbed again.

The capacity of the celluloid when well dried hardly altered at all with change of frequency and was much lower than when moisture was present; it also altered little with temperature. On the other hand, with moisture present it was larger almost in direct proportion to the amount of moisture present, and it altered considerably with change of frequency and with change of temperature.

The same actions occur in other dielectrics, liquid and solid, in different degrees. Corresponding changes also take place in the losses in both alternating and steady fields, and of these the losses in alternating fields seem more proportionate to the amount of moisture present than those in steady fields, especially when the amount of moisture is under 1 per cent.

These results appear to be very closely the same in principle as those obtained by the author with electrolytes, though the magnitudes and relative proportions of the quantities obtained may vary widely.

It does not seem difficult to find a general explanation of these results in both cases if we take in the first place the modern electronic theory of matter and the known facts of ionisation.

The modern view of the molecule as formed of a positive nucleus and negatively charged electrons surrounding it at once gives us a fundamental capacity effect as it is called; that is when these molecules are put in an electric field the positive nucleus is attracted in one direction and the negative electrons in the opposite. Their arrangement is therefore deformed, leading to a lock-up of energy; this then remains stable as long as the field is maintained, without further expenditure. When the field is taken away the molecules relapse to their former positions and the stored energy is given up, and this forms the discharge. If we suppose that amongst the molecules of the substance are mixed a certain proportion of ions formed from moisture or other electrolytes, they also will have positive and negative charges and will be affected in the same way as the fundamental molecules; but in this case the ions are separate positive and negative entities and are mobile and the field tends to draw them through the material towards the two surfaces; there will be resistance to this motion proportionate to its extent, and this constitutes the losses which are observed; also as the ions approach the surfaces more energy will be absorbed and the capacity appears higher, this varying with time. When the field is taken away these ions will relapse to their former positions more or less slowly, giving up their charge, but showing losses in doing so, which vary with the frequency.

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This is the explanation I gave in my lectures at the Institution of Electrical Engineers last year, and which I have discussed with friends from time to time. The only serious objection which has so far been raised is the question whether all the losses are occasioned in this way, or whether a part are fundamental to the material itself; and, if so, how much in each case.

Professor J. R. Partington (*communicated*).

The discussion of the factors which regulate the apparent resistance of an electrolytic cell, as presented by Dr. Haworth, appears to me to neglect the most important, namely polarisation. A current flowing for a short time in one direction will tend to deposit a layer of ions on each of the electrodes, and the opposing E.M.F. of this layer will increase the resistance of the cell. The higher the frequency of the applied E.M.F., the less deposition will occur, and the smaller will be the increase of resistance. This matter is considered in detail by Kohlrausch and Holborn (*Leitvermögen der Elektrolyte*, 2nd edition, 1916). The polarisation is inversely proportional to the area of the electrodes, and therefore depends on the nature of the surface (platinised or unplatinised) of the latter. I do not know whether this factor would explain all the observations of Dr. Haworth, but it is evident that until he has taken it into account it is premature to seek for other causes.

Dr. H. F. Haworth (*reply received November* 26, 1920): The significance of the vector diagram on page 374 seems to have been somewhat missed by the critics of the paper. The electrolytic cell is shown as a capacity in series with a resistance because that is the way it appears in the bridge measurements. If we consider the electrodes to act like leaky condensers with reference to the electrolyte, then if I_1 be the capacity current and I_2 be the leak current, $I = I_1 + I_2$ is equal to the total current through the electrolyte. If I_1 be now assumed constant, AR represents vectorially to some scale $2I_2r$, or $2I_1/Cw$, where r and C are the resistance and capacity of the condenser, and both are functions of the frequency. For the angle BAR to be independent of frequency means that $\tan BAR = \frac{I_2}{I_1}$. If we take the modern view of the molecule, as expressed by Mr. Addenbrooke in the discussion, the above result means that the ratio of the capacity current produced by the orientation on the molecules in the electric field, to the leak or direct conductivity current due to the mobile ions, is a constant quantity.

The impedances of the electrolytic condensers at infinite frequency are zero, and the resistances of the double layers on the electrodes does not appear in the extrapolated resistance as suggested by Professor Porter.

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THE MEASUREMENT OF ELECTRICAL CONDUCTIVITY IN METALS AND ALLOYS AT HIGH TEMPERATURES.

By JOHN L. HAUGHTON, D.Sc.,

FROM THE NATIONAL PHYSICAL LABORATORY.

A Paper read before THE FARADAY SOCIETY, *June* 14, 1920, PROFESSOR ALFRED W. PORTER, D.Sc., F.R.S., VICE-PRESIDENT, *in the Chair.*)

The measurement of electrical conductivity of metals at ordinary temperatures has been carried to such a degree of perfection that it is comparable in accuracy with the measurement of mass or of length. Such determinations have been carried out, probably with but small loss of accuracy, at temperatures of the order of 100° C. by immersing the specimen in an oil bath. The measurement of conductivity at much higher temperatures—up to 1,000° C.—has, however, not received nearly as much attention, and the purpose of this paper is to describe an apparatus with which such determinations can readily be carried out.

The apparatus was designed primarily to determine the electrical conductivity of a series of alloys at varying temperatures with a view to obtaining some information on their constitution. The whole theory of the study of electrical conductivity of alloys as an aid to the establishment of their equilibrium diagrams has been very fully discussed by Guertler,* and it is only necessary to state that this method, as well as the study of certain other physical properties, has the great advantage that measurements can be carried out as slowly as may be necessary to attain complete equilibrium. This is manifestly impossible in the case of thermal analysis, as there is a minimum speed at which thermal curves can be taken, a speed determined partly by the inaccuracy introduced in timing a very slowly moving galvanometer spot, and partly by the exceedingly small effect produced by a small heat evolution spread over a long time. This applies to any set of observations relating to a rate of change, as is the case in thermal curves, and not a steady condition, as in the case of electrical conductivity. In addition to this, the use of thermal curves is limited to the determination of phase boundaries which do not depart very markedly from the horizontal—limits of solubility, for example, can rarely be detected on thermal curves—while this is not the case with electrical conductivity measurements.

It must not be inferred from these remarks that the author considers that the electrical conductivity method is likely to supersede the thermal curve method as an implement for determining the constitution of alloys. On the contrary, he is convinced that the

* W. Guertler. *The Electrical Conductivity and Constitution of Alloys. Jnl. Inst. Met.*, Vol. 6 (1911), p. 135.

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most important place will always be shared by the method of thermal analysis and the examination of annealed and quenched specimens by the microscope. The majority of reactions occur sufficiently readily for their temperature to be determined by a comparison of heating and cooling curves. Thermal curves can be taken so quickly, easily and accurately, provided suitable methods are employed with reasonable care, that it is probable that the thermal method will always be of prime importance in the investigation of alloy systems.

The determination of the specific conductivity of a series of alloys at a certain temperature, while giving very valuable results, has but a limited application, for it is necessary to know the dimensions of the specimen accurately in order to determine the specific conductivity. To secure this, it is necessary not only to obtain the specimen in a form suitable for accurate measurement, but also to secure the absence of blowholes, and in practice this limits the application of the method to those alloys which can be drawn or rolled, or at least machined. But, instead of measuring the specific conductivity, it is possible to measure the temperature coefficient of electrical resistance of the alloys, and this can be done without any knowledge of the dimensions of the sample. The curve connecting temperature coefficient and composition is then plotted, and breaks in this curve indicate the composition at which phase changes occur in the alloys. Another method is to observe the conductivity at a number of temperatures, and to plot a curve connecting conductivity and temperature. Changes in the direction of this curve show the temperatures of phase changes in the alloy, and if a series of such curves be taken with different alloys, the points thus obtained can be plotted on the equilibrium diagram in the same way as points obtained from thermal curves.

The methods of measuring electrical conductivity at ordinary temperatures need not be dealt with here, as reference can be made to any text book on electricity for a description of the methods employed. For use in constitutional work, the problem is simplified by the fact that absolute values are, generally, not required, but is much complicated by the necessity of working at high temperatures. The difficulties introduced by this arise from the necessity of obtaining uniformity of temperature in the specimen, and from the fact that there is an unavoidable temperature gradient in the leads to the specimen.

The apparatus described below was designed by the author, and has been in use in the Metallurgy Department of the National Physical Laboratory during the past year with considerable success.

The principle on which the apparatus works is the measurement of the voltage drop along a fixed length of the specimen, through which a constant current is passing. This voltage drop is proportional to the resistance between the points of contact so long as the current is kept constant. In order to ensure this, the same current is passed through a constantan strip, whose resistance can be arranged to be of the same order as that of the specimen, and is accurately known, and the voltage drop along this resistance is measured with the same instrument and almost at the same time as that along the specimen. In this way, not only is the constancy of current checked (this being adjusted by means of a rheostat when necessary), but

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also the instrument which is reading the voltage drop is calibrated directly in some multiple of ohms. The details of the arrangement are as follows. The specimen (which is in a specially designed furnace) is in series with a standard resistance and a 2-volt accumulator. By means of a potentiometer or a galvanometer, the voltage drop across the specimen is compared with that across the standard resistance. The connections are shown diagrammatically in Fig. 1, where Rx represents the specimen whose conductivity is to be measured. B is a 2-volt accumulator sending a current through an ammeter M, a series of resistances Rf and a low resistance slide wire Rv for regulating the current, a standard resistance Rs, a switch S,

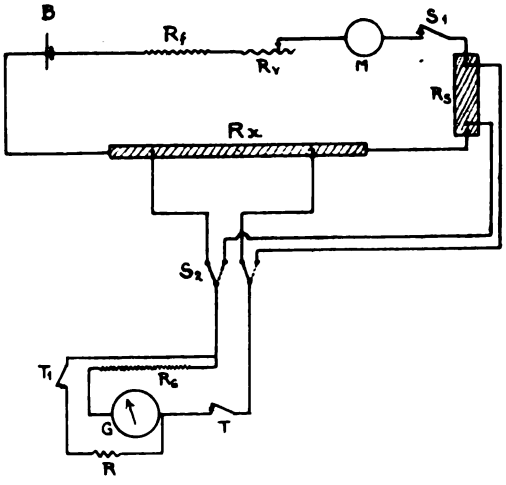

FIG. 1.

and the specimen Rx. From two fixed points on Rs, whose distance apart is such that the resistance between them is 0.002 ohms, wires are led to a two-way, double-pole switch S_2.* Two leads from fixed points in the specimen Rx are also connected to this switch, by means of which either these leads or the wires from Rs can be connected to a potentiometer or galvanometer and the voltage drop across Rs compared with that across Rx. While the use of a potentiometer is probably to be recommended where absolute values are required, or where a very high accuracy is sought (particularly if the resistance of the specimen and the standard are very different), the galvanometer is much easier to operate, especially when the resistance of the specimen is much affected by small changes of temperature. Obtaining a balance on the potentiometer takes very much longer than reading a galvanometer deflection. This is of some importance, as the accuracy of the method depends, amongst other things, upon the assumption that the current from the accumulator

* Other tappings, giving different resistances, are also taken from Rs, but, for the sake of simplifying the description, only this one is referred to here. The resistance used should be of the same order as that of the specimen.

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does not change between the readings of Rs and Rx: the time between these readings should therefore be kept as short as possible. The galvanometer circuit contains a tumbler switch T and a resistance Rg, of about 1,500 ohms; the galvanometer can be shunted through a further small resistance R by means of the switch T_1.

Fig. 2 is a wiring diagram of the apparatus, the wires below the board on which the apparatus is mounted being shown in dotted lines.

It is of the utmost importance that the potential leads from Rs and Rx should be thoroughly insulated from all other leads, as any leakage would be fatal to accuracy. To ensure this, all the leads on the apparatus consist of very heavily insulated copper wire, and even the insulation of the potential leads is not allowed to come into contact with the other wires or with the board on which the apparatus is mounted. All terminals are carried on ebonite blocks, those connected to the potential leads being on separate blocks from the others. The accumulator stands in a trough of paraffin wax.

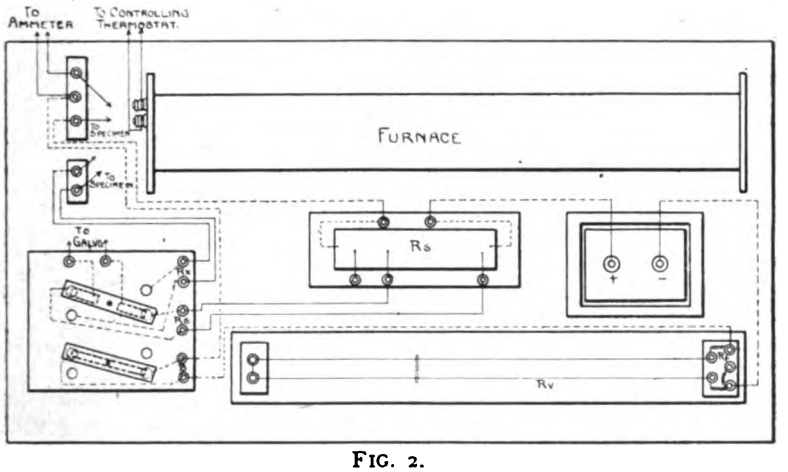

FIG. 2.

The apparatus is used as follows:—When the specimen, which is in the special furnace described below, is at the desired temperature, the two-way switch S_2 is set so that it connects the standard resistance, Rs, with the galvanometer circuit, whose switch, T, is then closed. The resistances Rf and Rv are then adjusted until such a current is flowing that the drop of potential across the 0.002 ohms of Rs causes a deflection of the galvanometer spot of 200 divisions. When this is so, one scale division is equal to 10^{-5} ohms. The switch T is then opened, S_2 switched over to the leads from the specimen, and T_1 and T closed. The object of T_1 is to protect the galvanometer from injury in the event of the specimen being broken, in which case the full voltage from the battery would be applied to the galvanometer terminals. If the specimen be intact, the deflection indicated by the galvanometer is very small, and T_1 may be opened. The galvanometer deflection will then give the resistance of the specimen in hundredths of a milli-ohm $\pm$ the sum of the various

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currents due to thermal electromotive forces in the circuit. In order to find what is the effect of these, the switch S_1 is now opened, and any deflection of the galvanometer will be due to the combined or opposed effects of the thermal E.M.F.s. The value of this deflection is applied as a correction (either additive or subtractive, as the case may be), to the value obtained for the resistance of the specimen. When the rate of heating or cooling is slow, this correction is rarely greater than one or two scale divisions with the furnace described below, but if the rate of change of temperature be very great, a much larger correction may be found, probably due to a temperature gradient in the specimen. The presence of any thermal E.M.F. in the circuit from the standard resistance is observed by switching S_2 on the standard resistance and noting the deflection obtained on the galvanometer scale while S_1 is open. Generally speaking, this does not exceed half a division.

The temperature of the specimen is measured by means of a thermo-couple placed at the middle of the specimen and connected to a potentiometer. The scale of the galvanometer used with this potentiometer is placed above the one belonging to the conductivity galvanometer, and the readings are taken in the following order:—

(1) The temperature.
(2) The deflection due to the potential drop in Rs.
(3) The deflection due to the potential drop in Rx.
(4) The thermal E.M.F. in Rx.
(5) The temperature.

Readings (1) and (5) should be the same.

If the deflection due to the potential drop in Rs has altered by a very small amount from the original setting, a correction can be applied to the reading of Rx, but it is best to keep the reading of Rs as near its correct value as possible.

It may be well at this point to consider the comparative merits of this method of measuring resistance with other possible ones.

(1) The resistance of a circuit can be determined by measuring the current produced in the circuit on the application of a definite E.M.F. to the ends of the circuit. Since, however, the measuring instruments must be outside the furnace, the circuit must include leads to the instruments, and these would have a temperature gradient in them. This would render it extremely difficult to calculate the correction which would be required for the resistance of the leads. Further, the resistance of the specimen would, in general, have to be small compared with the resistance of the leads, as it is necessary to use a specimen which is very short compared with the length of the furnace if a high degree of temperature uniformity is required in the former. Thus we have to measure the change in a small resistance by measuring the change in the sum of this small resistance + a much larger one, which itself is changing. This is by no means an ideal condition. It would be possible to have a dummy lead passing through the furnace close to the other leads and as similar to them in every respect as possible, and by measuring the resistance of these dummy leads almost at the same time as the resistance of the real leads and the specimen to deduce the resistance of the specimen, but this introduces possibilities of serious errors. Slight resistances at contacts anywhere in the circuit will also introduce

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very large errors, as in this method the total resistance of the circuit must be kept low. In the potentialdrop method, on the other hand, the total resistance in the galvanometer circuit may be many hundreds of ohms, and therefore the introduction of a small resistance in the lead is negligible.

(2) A much better way of measuring the resistance of a circuit than the voltmeter-ammeter method is the use of a bridge—preferably, in the case where the resistance is small, a Kelvin double bridge. This method has one advantage over that described in this paper, viz., that the constancy of the current flowing through the circuit is unimportant. Indeed, where accurate absolute values are required, it is probable that it would be the right method to use. On the other hand, to get a hgh sensitivity, it s necessary to pass a comparatvely heavy current through the specimen. This will introduce considerable difficulties, and probable errors, in the measurement of the temperature of the specimen. The use of a heavy current will also increase the probable errors due to Peltier and Thomson effects.

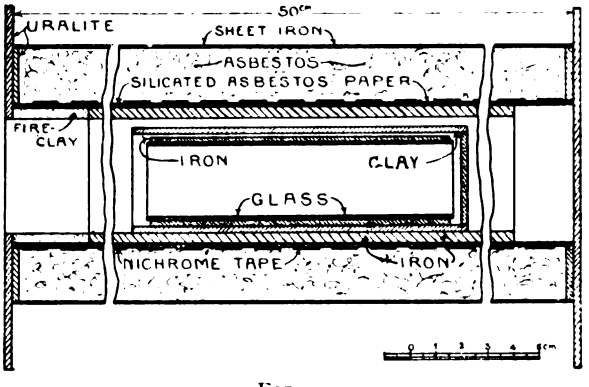

FIG. 3.

It is of the utmost importance that the temperature of the specimen should be as uniform as possible along its whole length, and to ensure this the furnace described below was designed. The use of iron in its construction limits its use to temperatures not exceeding about 700° C., but for higher temperatures this can be replaced by an alloy, such as "nichrome," designed to stand high temperatures.

The furnace consists of an iron tube 5 cm. in diameter and 45 cm long, over which are wrapped several layers of asbestos paper soaked in sodium silicate. (Fig. 3.) This wrapping projects well beyond the end of the iron tube, and, when the sodium silicate is dry, has sufficient rigidity to carry a winding of nichrome tape, even where it is not supported by the iron. The whole furnace is enclosed in a casing of iron 10 cm. in diameter, the space between this and the asbestos tube being filled with magnesia lagging. By thus carrying the winding well beyond the iron tube, the end effect is considerably reduced, and this, together with the comparatively good thermal conductivity of the iron, gives to the furnace a reasonable

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degree of uniformity of temperature. Indeed, the temperature was found to be constant to 1° C. over a length of 11 cms., the measurements being made by means of a base-metal thermo-couple in the empty furnace.

It has been shown by Kelvin and others that the best way to obtain a uniform temperature in an enclosed space is to have a series of alternate conductors and insulators between the source of heat and the space—a principle which has been partially carried out in this furnace. Inside the iron tube, which is a heat conductor, surrounded by the insulating asbestos, is a clay tube 13 cms. long, one end of which is permanently closed. Within this is an iron tube, a little shorter than the clay one, into which fits another clay or glass

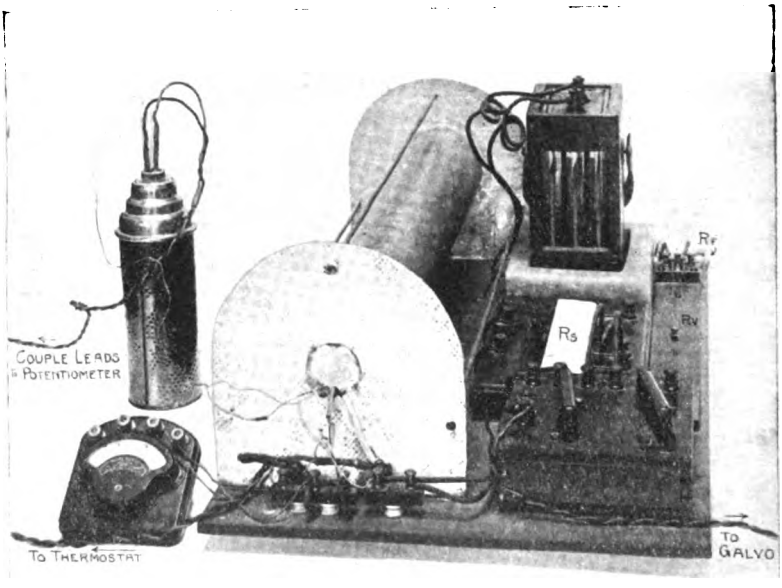

FIG 4.

tube. The specimen whose temperature-conductivity curve is required, is placed, together with the various leads, thermo-couple, etc., inside the innermost tube, and the open end of the outer clay tube is plugged up with asbestos wool, as is the mouth of the furnace. With the specimen described below, the temperature of the furnace tube varies by 0.5° C. over the length of the specimen, but the temperature gradient in the specimen itself will be very much less.

The temperature of the furnace can be controlled by hand by means of an external resistance, but a preferable method is to connect it in parallel with a thermostat whose temperature is caused to fall slowly by the method described by Mr. Hanson and the author in an earlier paper.*

A photograph of the apparatus is shown in Fig. 4.

* *Further Notes on a High Temperature Thermostat.* Haughton and Hanson. *Journal of the Institution of Metals*, Vol. 18, No. 2, 1917, p. 17.

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Various forms of specimens have been used. Where possible the metal was cast into a rod from which a sample, of the shape shown in Fig. 5, was turned. Small iron rods were screwed into the specimen in the positions marked AA and BB, and to the former the current leads were soldered with silver solder, while the potential leads were similarly attached to BB.

Specimens of this shape are not suitable or are unobtainable, when it is desired to extend the temperature-conductivity curve above the solidus, or when the specimen is not machinable. Attempts were made to suck the metal (in the case of low melting point alloys) into a glass tube into the sides of which four platinum wires had been sealed. This was not very satisfactory, as it was found exceedingly difficult to avoid fracturing the glass either during filling or in the subsequent cooling. The best method used consisted in casting a rod about 2 mm. in diameter, and firmly binding on to this four pieces of fine wire (platinum, copper and constantan have been used, according to the circumstances). When the melting temperature of the alloy was to be exceeded, the specimen and the wires were given a wash of " Purimachos " cement and, when this had set, further coats of the cement were put on until a solid tube was

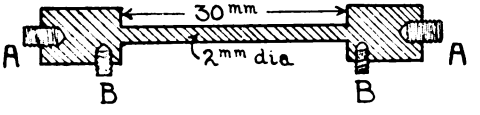

FIG. 5.

built round the specimen. This was then placed inside the innermost tube in the furnace, which was packed with powdered china clay to reinforce the " Purimachos " tube. This method was found perfectly satisfactory.

The casting of the rods was carried out in two or three different ways, but perhaps the most satisfactory was found to be a method due to Broniewski. This consists in placing some lumps of the metal whose resistance is to be determined in a crucible, into which is inserted the end of a tube of silica or glass, the other end of which is sealed up. The crucible and tube are then placed in a suitably designed electric resistance furnace, and the whole is placed in a vessel which can be evacuated. The air is pumped out of the apparatus, and, as the end of the tube is open in the crucible, this is also evacuated. The furnace is then switched on, and when the alloy melts, the open end of the tube sinks below the surface of the liquid metal. (If necessary, the tube can be weighted to ensure this sinking.) Air is then admitted into the vessel, and the molten metal is thereby forced up into the tube. The latter is then removed from the furnace, and is broken off the specimen, which remains in the form of a rod of the same diameter as the bore of the tube.

The majority of the work which has been done with this apparatus is in connection with the investigation of alloy systems, the results of which are about to be published elsewhere. It is therefore not possible to give many illustrations of the results obtained, but reference may be made to two.

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In an investigation of the constitution of the copper-aluminium-zinc alloys it was found that the liquidus and solidus occur, over a short range, so close together that it was not possible to distinguish between them by means of thermal curves. The liquidus was determined by this means, and the solidus by quenchings, but this meant that the determination of the two lines was carried out on different samples, by different methods, and the various errors introduced might all be additive. Electrical conductivity measure-

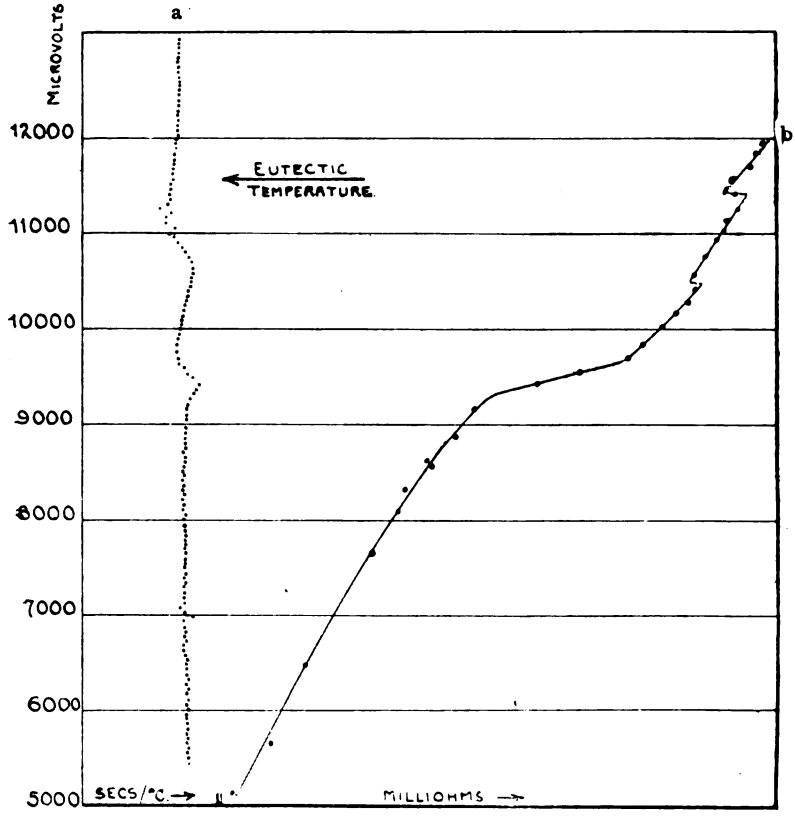

FIG. 6

ments, however, showed marked changes in the direction of the curve connecting conductivity and temperature at both the solidus and the liquidus, and served as a valuable check on the other determinations.

In Fig. 6 a is a thermal curve (heating) of a copper-tin alloy containing about 60 per cent. of tin, and b is an electrical conductivity curve of the same alloy. It will be seen that the latter has three breaks; two of them are also shown in the thermal curve; the lower one of these is probably due to an allotropic modification in one of the constituents of the alloy. The meaning of the other is not clear. The third point on the electrical conductivity curve,

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which does not show on the thermal curve, is of particular interest. It occurs at the eutectic temperature of the system. Microscopic examination shows that there are the merest traces of eutectic present in the alloy—not nearly enough to show on the thermal curve, but it can readily be seen on the conductivity curve.

In conclusion the author wishes to express his thanks to Dr. Rosenhain, F.R.S., for his interest in the work, and to Mr. Albert Campbell and Mr. S. W. Melson for their advice in connection with the method used for measuring the resistance.

Discussion.

The Chairman said he did not quite gather what was the chief novelty claimed for the method. It appeared to him that it was an ordinary method of measuring resistance on the lines of the potentiometer method. He was not sure to what extent the ends of the specimen were at the same temperature as the main body.

Dr. Haughton said the temperature was very nearly uniform all along the specimen.

Dr. Haughton wrote (*received November* 26, 1920) with regard to the Chairman's remarks, that he did not claim any novelty in the principle described in the paper. It was rather in the details of the way the principle was applied. He had had to carry out electrical conductivity measurements at high temperatures, and had found no description of a method for doing this, so he devised the apparatus described in this paper. This took some time and thought, and considerable modifications were introduced in the apparatus as first designed, before it was really satisfactory. In order to save other workers from having to go through this stage of experimenting, he described the final result at which he had arrived.

With regard to the temperature gradient in the specimen, this was very small. As was stated in the paper, the temperature of the furnace tube did not vary by more than 0.5° C. over the length of the specimen. Owing to the way the latter was packed in the furnace, it is probable that there was not a temperature difference as great as 0.1° C. between any two parts of the specimen.

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THE THEORY OF ELECTROCHEMICAL CHLORATE AND PERCHLORATE FORMATION.

By N. V. S. KNIBBS AND H. PALFREEMAN.

(*A Paper read before* THE FARADAY SOCIETY, *June* 14, 1920, PROFESSOR ALFRED W. PORTER, D.Sc., F.R.S., VICE-PRESIDENT, *in the Chair.*)

Introduction.

This paper is the outcome of a study of the electrolytic formation of chlorate and perchlorate based on recent large scale operations. It aims at a presentation of the theory of the mechanism of chlorate and perchlorate formation and its application to their technical production. A series of investigations was undertaken in order to elucidate a number of doubtful points and to obtain data which were of importance in the technical control of the process, but these investigations were cut short by the termination of operations, and therefore are incomplete in many respects.

The paper is divided into three parts. Part I contains an account of some of the experimental work. It gives the results of the measurement of the conductivities of chlorate, chloride-chlorate, perchlorate, and chlorate-perchlorate solutions, the velocity constants of the reaction: hypochlorite to chlorate, and the resistance and potential effects in technical cells. It is believed that the data on conductivities and on the dynamics of the hypochlorite-chlorate reaction cover a wider range than any that have previously been published. Part II deals with chlorate formation, and after a survey of the generally accepted theory, the efficiency of the process is discussed in some detail. In Part III, dealing with perchlorate formation, the two most important suggestions that have been made as to the mechanism of the process are discussed, and a modified theory proposed. Several experimental investigations not included in Part I are briefly referred to in Parts II and III, but they are the joint work of the authors of Part I.

The paper is concerned largely with the factors in technical efficiency, but it treats the subject quite generally, and no attempt is made to give working details. A general description of the process and of some of the technical cells will be found in the books tabulated in the bibliography which is appended.

PART I.—EXPERIMENTAL.

By N. V. S. KNIBBS AND H. PALFREEMAN.

Conductivity.

A series of conductivity measurements was made of pure chlorate solutions, mixtures of chloride and chlorate, and of chlorate and perchlorate; also, a limited number on pure perchlorate solutions.

The measurements were carried out with the usual conductivity apparatus, using a telephone. Two resistances of 1,000 ohms each formed two arms of the bridge, whilst an adjustable resistance of

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the dial type (Paul), reading from 1 to 11,110 ohms, was balanced against the conductivity cell. By changing the cell as the temperature was raised, the resistance was always kept above 300 ohms, and adjustment to 1 ohm was easily made. The usual type of conductivity cell for electrolytes of low resistance was employed, and several such cells were made, having different constants, in order to maintain the resistance within the required range at the various temperatures. The electrodes were platinised discs of platinum, 0.5 inch in diameter. The cell constants were obtained at all temperatures and at frequent intervals throughout the measurements, using normal KCl. With Kolhrausch's temperature coefficient the variation of the cell constant with temperature was small. It is evident, however, that at high temperatures there is some uncertainty as to the actual conductivity of the potassium chloride solution used as standard. The conductivity cell was immersed in a thermostat which at all temperatures up to 60° was kept within 0°.1. Above 60° the variation was sometimes wider, but never above 0°.2.

The salts used in making up the solutions were of considerable purity. The sodium chloride was a pure Merck product, whilst the chlorate was recrystallised three times from the crude salt, and contained in all cases less than 0.005 per cent. NaCl—the chief impurity. The perchlorate was twice recrystallised, and contained less than .02 per cent. of both chlorate and chloride. Ordinary pure distilled water was used, the high conductivity of the solutions rendering the use of conductivity water unnecessary. All solutions except those in which the total quantity of salt was not soluble at that temperature were made up at 20°. Those which required a higher temperature were made up at the lowest possible temperature at which they would dissolve (*i.e.*, at 30°, 40°, 50°, or 60°). It is evident that these are not quite equivalent to those made up at 20°, and if it were possible to cool them to 20° they would contain more than the stated number of grams per litre of salt.

High accuracy is not claimed for these measurements, which were made for technical purposes. The number of measurements were large, and the time at our disposal short. At low temperatures, however, the error is not great, as may be seen by a comparison with Heydweiller's measurements of chlorate at 18°, our figures agreeing to within 1 per cent.

At high temperatures, say over 60°, the thermostat was not quite as constant as below this temperature, and other errors operated such as that due to evaporation in the cell during the attainment of the thermostat temperature. The nature of increase of conductivity with temperature shows, however, that the error cannot be very large, and certainly the measurements are well within the limits of accuracy required for technical application.

The increase of conductivity with temperature is in all cases nearly linear, and it is within the limits of accuracy of the measurements to assume a linear increase between any two temperatures, and calculate the values for an intermediate temperature by interpolation.

In the case of chlorate, solutions were prepared of 100, 200, etc., up to 600 g/l, with intermediate strengths at the higher concentrations, also higher concentrations at 40°—60°. Readings were

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taken each 10 degrees from 20°—60°. The conductivity passes through a maximum value which varies between 530 g/l at 20° and 600 g/l at 60°. The increase of conductivity with temperature is nearly linear, and it will be seen that with increasing concentration the rate of increase with temperature becomes greater. Thus, a solution containing 600 g/l has a lower conductivity at 0° than solutions containing 400 and 500 g/l, but at 60° its conductivity is greater than either. For technical purposes higher temperatures than 60° would rarely be required, but the linear nature of the conductivity increase makes it possible to extrapolate above this temperature with considerable accuracy.

The conductivities of various mixtures of chlorate and chloride were determined at every 20 degrees between 20° and 80°. In most cases the solutions were prepared with intervals of 50 g/l chlorate for each chloride concentration. Within the range of concentration usually worked to in technical practice the measurements made were numerous, with 10 g/l intervals in the chloride concentrations. The increase with temperature is in all cases nearly linear, so that intermediate temperatures may be calculated with accuracy. Intermediate concentrations cannot be calculated with the same accuracy, but they will be well within the requirements of technical practice.

The limitation of the available time made it impossible to carry out measurements on which to base chlorate-perchlorate curves similar to those given for chloride-chlorate. Twelve measurements were, however, made at each temperature, and these are given below. They may be used to calculate the conductivity of any strong chlorate-perchlorate solution with sufficient accuracy for most technical purposes.

As a matter of interest the variation of conductivity of pure perchlorate solution with concentration up to 1,100 g/l was determined at 20° and 60°. The figures show maxima at nearly the same concentrations as the chlorate solution and a rapid fall at higher strengths.

Sodium Chlorate.

Concentration g/1.	20°	30°	40°	50°	60°
100	.062	.075	.089	.104	.118
150*	.085	.104	.123	.143	.162
200	.104	.126	.149	.174	.197
250*	.121	.145	.171	.200	.227
300	.134	.160	.189	.221	.250
350*	.143	.173	.204	.238	.270
400	.150	.182	.215	.250	.285
450*	.155	.187	.223	.260	.297
500	.157	.191	.227	.266	.303
550	.157	.192	.230	.268	.307
600	.155	.191	.231	.269	.308
650	.150	.188	.228	.266	.307
700	—	—	.226	.262	.303
750	—	—	.217	.256	.297

*Obtained from the curves plotted through the other points.

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Sodium Chloride—Sodium Chlorate.

Temp.	Chlorate g/l.	Chloride grams per litre.							
		25	50	100	110	120	130	140	150
20°	300	—	.159	—	.178	.180	.181	.182	.182
	350	—	.163	—	.176	.177	.178	.178	.179
	400	.158	.165	.172	.173	.173	.174	.174	.174
	450	.160	.165	.170	.169	.169	.168	.167	.166
	500	.161	.163	.166	.164	.162	.161	.159	.154
	550	.159	.160	.160	—	—	—	—	—
	600	.156	.155	.150	—	—	—	—	—
40°	300	—	.238	—	.259	.263	.266	.269	.271
	350	—	.242	—	.260	.264	.264	.265	.267
	400	.229	.243	.257	.260	.262	.260	.260	.262
	450	.233	.242	.255	.254	.253	.255	.253	.256*
	500	.237	.240	.252	.248	.248	.247	.244	.249*
	550	.236	.238	.247	.243	.243	—	—	—
	600	.233	.236	.238	.240*	.234	—	—	—
60°	300	—	.301	—	.345	.351	.356	.361	.364
	350	—	.313	—	.347	.354	.355	.359	.360
	400	.304	.320	.346	.347	.350	.352	.355	.357
	450	.310	.325	.344	.344	.345	.346	.348	.350
	500	.315	.325	.342	.336	.338	.340	.340	.343
	550	.316	.325	.334	.333	.334	—	—	—
	600	.315	.323	.325	.330	.326	—	—	—
80°	300	—	.382	—	.440	.447	.453	.461	.465
	350	—	.396	—	.444	.449	.454	.459	.463
	400	.385	.406	.439	.444	.449	.453	.457	.460
	450	.394	.413	.437	.442	.445	.447	.453	.453
	500	.401	.416	.436	.438	.440	.441	.447*	.444
	550	.404	.416	.430	.434	.435	—	—	—
	600	.404	.411	.422	.430	.426	—	—	—

Chlorate g l.	Chloride g/l and Temperature.							
	20°		40°		60°		80°	
	200	250	200	250	200	250	200	250
50	—	.213	—	.304*	—	.411	—	.521
100	.199	.209	.287	.306	.381	.410	.483	.521
150	.198	.204	.289	.302	.384	.407	.491	.522
200	.196	—	.288	—	.386	—	.493	—
250	—	—	.280	—	.384	—	.491	—
300	—	—	.281	—	.381	—	.485	—

* The accuracy of these values would appear to be doubtful.

It will be observed that at moderate concentrations an increase of chlorate results in a decrease of conductivity, whilst an increase of chloride has the reverse effect. At higher concentration an increase of either salt reduces the conductivity, but the point of maxi-

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mum conductivity moves to higher concentrations with increase of temperature. It will also be seen that the substitution of chloride for an equivalent amount of chlorate in all cases results in a considerable increase of conductivity.

Sodium Chlorate—Sodium Perchlorate.

g l $NaClO_3$	g l $NaClO_4$	Conductivity. 20°	30°	40°	50°	60°
0	600	.166	.203	.244	.282	.325
0	800	.151	.189	.229	.269	.312
100	500	.164	.202	.240	.280	.322
100	700	.149	.186	.225	.266	.308
200	400	.162	.200	.238	.278	.319
200	600	147	.185	.224	.264	.306
300	300	.160	.198	.236	.276	.317
300	400	.155	.193	.230	.272	.314
400	150	.159	.195	233	.271	.311
400	250	.157	.194	.233	.272	.314
500	75	.157	193	.231	.269	.310
500	125	.156	.193	.231	.270	.312

Sodium Perchlorate.

Temp.	Perchlorate grams per litre. 200	400	500	600	700	800	900	1000	1100
20°	.102	.154	.164	.166	.162	.151	.137	.122	.105
60°	.192	.293	.316	.326	.325	.313	.296	.273	.247

Dynamics of the Reaction: Hypochlorite to Chlorate.

The reactions by which chlorate is formed from hypochlorite may be represented by the equations:—

$$OCl' + 2HOCl = ClO'_3 + 2H^{\cdot} + 2Cl'^{*}$$
$$2OCl' + 2H^{\cdot} + 2Cl' = 2HOCl' + 2Cl'$$

the net result being the disappearance of three hypochlorite ions (or sodium hypochlorite molecules) with the formation of one of chlorate and two of chloride. Direct reaction between hypochlorite ions or molecules does not seem to occur, except perhaps with low velocity, because in alkaline solution hypochlorite is stable. Hypochlorous acid, being very weak, will be only slightly ionised, hence, as long as there is sufficient hypochlorite present, the concentration of hypochlorous acid will remain appreciably constant. The reaction represented by the first equation is termolecular, but on account of the

* The action is reversible, but Sand [*Zeit. Physikal. Chem.* 50, 465 (1904)] found the constant for the forward reaction to be $k_{18} = 53$, whilst for the reverse reaction he found $k'_{18} = 0.56 \times 10^{-3}$. The conversion to chlorate will therefore be almost complete.

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constancy of hypochlorous acid, it will follow the course of a unimolecular reaction as long as there is enough hypochlorite present. The velocity of the re-formation of hypochlorous acid, represented by the second equation, is very great, and need not be considered. The velocity of the reaction should vary with the square of the hypochlorous acid concentration if the above equation is correct, and experiments were carried out to verify this and to determine the variation with change of temperature.

A solution of sodium hypochlorite (containing a large excess of chloride) was made by electrolysing pure chloride solution, and stabilised by the addition of a little alkali. The solution of the hypochlorite in a flask was suspended in the thermostat and allowed to attain constant temperature. Acid (normal sulphuric) was then added, and samples pipetted out at time intervals into potassium iodide solution, which was subsequently acidified with dilute hydrochloric acid and titrated with tenth normal thiosulphate. The titration gives the total hypochlorite content, including the hypochlorous acid, so that it is necessary to deduct the figure for the latter to obtain the sodium hypochlorite concentration alone. The hypochlorous acid could not be satisfactorily determined analytically. Several methods have been proposed, but none were found perfectly reliable. It was found that the addition of acid up to a certain quantity (slightly more than equivalent to the stabilising alkali which had been added) had no appreciable effect upon the velocity of the reaction, but that, after this quantity had been exceeded, the change at once became apparent. It was assumed that the acid added in excess of the above quantity resulted in the formation of an equivalent amount of hypochlorous acid. The low dissociation constant of hypochlorous acid makes this assumption justifiable, and the accuracy of the value obtained will depend upon the accuracy with which the point at which acid begins to be liberated can be determined. The assumption is made that the sodium hypochlorite is appreciably all dissociated, or alternatively that the ions and molecules react equally. It will be seen that this probably leads to error in high concentration.

Experimental Results.

The results of all determinations showed that the reaction gave a constant with the unimolecular formula as long as there was enough hypochlorite present. The full experimental figures are tabulated for the first set of determinations, and they may be taken as being representative.

All concentrations are given in gram-molecules per litre; time in minutes. Under " C.C." the titrations in cubic centimetres of decinormal thiosulphate are tabulated.

$$k = \frac{1}{t} \log_{10} \frac{a}{a - x}$$

where a and x refer to NaOCl only.

$$k' = \frac{1}{t} \log_e \frac{a}{a - x} = 2.30\ k.$$

$$K = \frac{k'}{[HOCl]^2}$$

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(1) Variation of k with concentration of HOCl at 80°.

[HOCl] = 0.002					[HOCl] = 0.008				
Time.	C.C.	NaOCl	Log.	k.	Time.	C.C.	NaOCl	Log.	k
0	63.3	0.3145	.4795	—	0	60.6	0.293	.4669	—
10	62.1	0.3185	.4893	0.00083	8.5	56.3	0.2715	.4338	.0041
22	61.2	0.304	.4829	.00053	14.5	53.5	0.2575	.4108	.0038
36	60.4	0.300	.4771	.00042	22	50.6	0.243	.3856	.0034
45	60.0	0.298	.4742	.00031	36	45.4	0.217	.3365	.0035
62	59.4	0.295	.4698	.00026	44	42.9	0.2045	.3107	.0032
96	58.0	0.288	.4594	.00031	62	36.8	0.174	.2405	.0039
136	56.0	0.280	.4472	.00030	90	29.3	0.1365	.1351	.0038
					132	20.0	0.090	.9542	.0043
					171	15.2	0.066	.8195	.0035
	k = 0.00030					k = 0.0037			

[HOCl] = 0.015.					[HOCl] = 0.022.				
Time	C.C.	NaOCl	Log.	k.	Time.	C.C.	NaOCl	Log.	k.
0	64.9	0.3095	.4907	—	0	55.0	0.253	.4031	—
13	47.2	0.221	.3444	0.0113	7.8	36.1	0.1585	.2000	0.026
27	23.0	0.100	.0000	0.0246	14	23.6	0.096	.9823	0.035
37	17.3	0.0715	.8543	0.0146	18	18.6	0.071	.8513	0.033
53	11.4	0.042	.6232	0.0144	23	14.0	0.048	.6812	0.034
63	9.0	0.030	.4771	0.0146	30	10.2	0.029	.4624	0.031
87	5.6	0.013	.1139	0.0151	37	6.8	0.012	.0792	0.052
133	3.2	—	—	—	62	3.6	—	—	—
164	2.5	—	—	—	172	1.9	—	—	—
	k=0.0147					k=0.033			

[HOCl] = 0.042.

Time.	C.C.	NaOCl	Log.	k.
0	49.8	0.207	.3160	—
3	25.3	0.0845	.9269	0.130
6 8	13.7	0.0265	.4232	0.132
17	6.6	—	—	—
37	5.8	—	—	—
62	4.4	—	—	—
172	1.9	—	—	—
	k=0.131			

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Comparing k and [HOCl] we have:—

HOCl :	0.002	0.008	0.015	0.022	0.042
k :	0.00030	0.0037	0.0147	0.033	0.131
$\frac{k}{[HOCl]^2}$:	75	58	65	68	74

(2) Variation of k and K with temperature.

Temp. :	40°	50°	60°	70°	80°
k :	0.0025	0.0056	0.0130	0.024	0.042
$\frac{k}{[HOCl]^2}$:	4.2	9.3	22	40	70
K :	9.6	21.5	50	92	161

The constants at 40° and 50° are probably less reliable than those at 60°—80°, because the velocity of the reaction at the former temperatures was not at any time quite constant. From 60° to 80° K may be represented by the formula:—

$$K = e^{0.60 + 0.056t}$$

where t is in °C. It gives too high results at 40° and 50°, but a formula of the type $\log \frac{K_2}{K_1} = A. \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ gives no better results at these temperatures, and does not fit the higher temperatures as well.

(3) Variation with HOCl concentration at 60°.

[HOCl] :	0.002	0.006	0.018	0.040	0.060
k ;	0.00007	0.00048	0.0070	0.034	0.090
$\frac{k}{[HOCl]^2}$:	—	14	22	21	25

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(4) Variation with HOCl concentration at 30°.

[HOCl]	0.002	0.012	0.022	0.032	0.042
k	0.00004	0.00047	0.0017	0.0025	0.0040
$\frac{k}{[HOCl]^2}$	10	3.3	3.5	2.4	2.3

These results were variable, and k tended to increase throughout each measurement.

It was found in (2) that the value of $k\,[HOCl]^2$ at 80° is 70, at 60°: 22 and at 30° it would be expected to be about 2.0 to 2.5. Comparing with the other determinations, in (1) an average of 68 was found, in (3) an average of 23 (omitting the low figure for [HOCl] = 0.006, which is unreliable), and in (4) an average of 2.9 (or 2.35 for the higher acidities). The agreement, except at 30°, is good.

The rate of change of hypochlorite to chlorate at any moment is given by:—

$$\frac{dx}{dt} = k' \times \text{Conc. of NaOCl}$$
$$= K.\,[HOCl]^2\,[NaOCl]$$
$$= e^{0.60+0.056t}\,[HOCl]^2\,[NaOCl] \text{ above } 60°,$$

or K may be read off on diagram A, which is extrapolated up to 90°.

Diagram A also shows a set of curves of the decrease in hypochlorite (as given by the ccs. of thiosulphate used) for different acidities at 80°. The curves for high hypochlorous acid content are not asymptotic to the time axis, as would be expected if the titration gave directly the NaOCl concentration. They tend to become parallel to this axis at a distance above it, which is approximately equivalent to the hypochlorous acid concentration. They are not, however, quite parallel, probably because there is a slow change in the acid itself, and also because some of it is lost by volatilisation.

The reaction was investigated by Foerster,* who showed that the velocity is proportional to the square of the hypochlorous acid concentration, and conforms to the unimolecular formula. The values obtained for k were constant for dilute solutions, but with higher concentration the hypochlorite is initially not sufficiently completely dissociated. This may account for the results obtained at low temperatures when k increased slightly throughout, and if this is the explanation, the results would be too low at these temperatures. Foerster also showed that the reaction is accelerated by light and by the presence of chloride. He made no determinations above 49°. It may here be pointed out that the value $k = 0.0023$ at 25°, which has been quoted† as that of K in the equation $\frac{dx}{dt} = K\,[HOCl]^2$

* *J. prakt. Chem.* 63. 141 (1901).

† *e.g.*, Allmand, *Principles of Applied Electro-Chemistry*, p. 320.

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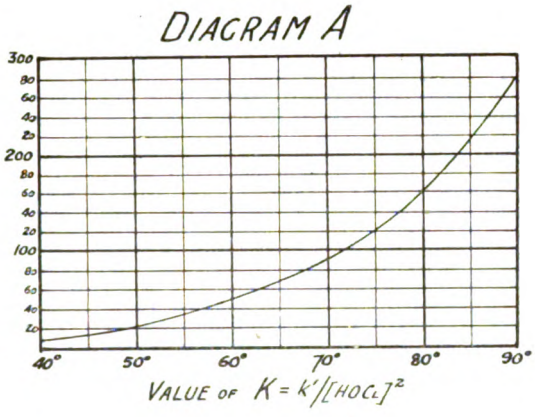
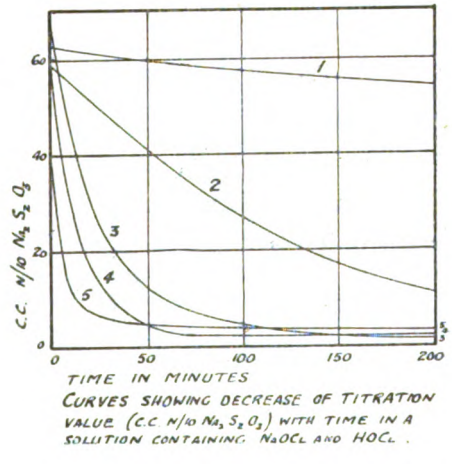
$[OCl']$ is really the equivalent of the k in our determinations, and, as shown above, $K = 2.30\ k/\ [HOCl]^2$.





CURVES SHOWING DECREASE OF TITRATION VALUE (c.c. N/10 $Na_2S_2O_3$) WITH TIME IN A SOLUTION CONTAINING $NaOCl$ AND $HOCl$.

Foerster gives the following values for $k = \frac{1}{t} \log. \frac{a}{a-x}$

19.5°	$k = 0.00133$	$[HOCl] = 0.0560$*
35°	0.0055	0.0585
49°	0.0205	0.0585

and from these it may be calculated that:—

$K = 0.97$ at 19.5°
3.71 ,, 35°
13.8 ,, 49°

It will be observed that these are considerably lower than the values obtained in the above experiments, but the increase with rise of temperature is more rapid, and extrapolation to 70° leads to a

* His HOCl concentrations are left in c.c. As_2O_3 sol. (N/10) in his calculation of $k/[HOCl]^2$.

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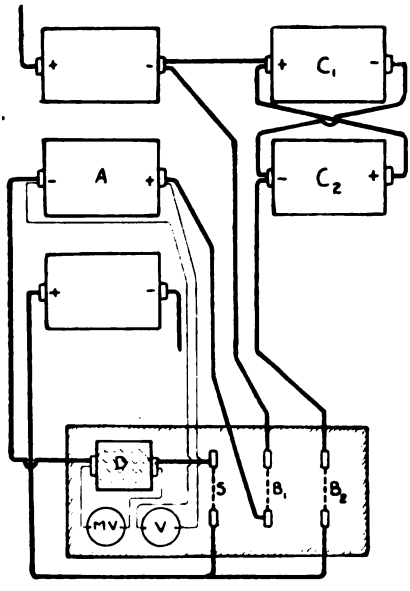
figure very nearly the same. Lower values are to be expected, because there was no excess of chloride present, and chloride was shown by Foerster to accelerate the reaction. It is also worth noting that he used the hydrogen peroxide method for the determination of the hypochlorous acid concentration: a method which was found rather unreliable.

Sand,* who made two determinations of the velocity at 70° and one at 20°, obtained still lower figures for K, namely: $K_{20} = 0.616$, $K_{70} = 53.1$.

DIAGRAM B



S · KNIFE SWITCH — MV · MILLIVOLTMETER
B1, B2 · CIRCUIT BREAKERS — V : VOLTMETER
D · STANDARD RESISTANCE — A · EXPERIMENTAL CELL
C1, C2 : RESISTANCE CELLS.

Resistance and Electrode Potentials of Technical Chlorate and Perchlorate Cells.

The voltage to be applied to a cell to produce a given current is determined by the ohmic resistance in the cell and the electrode potential effects. Without making any assumption as to the nature of the latter, the potential drop due to each of these two factors may be determined. If E be the total *e.m.f.* of the cell and E' the sum of the electrode potentials, then $E = CR + E'$. E and C

* *Zeit. physikal Chem.* 50, 465 (1904).

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may be measured, and if C be altered and the new values of E and C measured, R and E′ are obtained, assuming them to remain constant. Suppose, further, that it is possible quickly to switch the cell out of circuit. A certain back *e.m.f.* will be exerted by the electrodes, which can be read off on a voltmeter. Call this E_a, and if it is less than E′ the latter may be divided into $E_a + E_b$ and E_b obtained by difference. It has been found that a well-defined *e.m.f.* E_a (less than E) is exerted on isolating a cell.

To carry out the measurements a special movable switch panel was made, consisting of one knife switch and two circuit breakers, designed to carry heavy currents. A standard resistance was also fixed to the panel in series with a knife switch, and with a millivoltmeter it constituted a standard ammeter. The arrangement is reflected in diagram B. Connected to the switch and breakers were suitable lengths of flexible cable for the purpose of connecting up to the cells. In order to read the voltage of the cell, wires were soldered to anode and cathode, and connected to a standard voltmeter. The resistance, millivoltmeter, and voltmeter were Weston laboratory standard instruments.

The cell on which measurements were to be made was connected up to the switchboard as shown in the diagram. Two other cells in the adjoining row were also connected to the board, and filled with liquor of different strengths, to have different resistances. Then, by suitable manipulation of the connection and switches, the current in the experimental cell may be suddenly altered by putting one or both of C_1 and C_2 in parallel. It may also be isolated and its back *e.m.f.* recorded. R and E are calculated by means of the relations:—

$$R = \frac{E_1 - E_2}{C_1 - C_2} \qquad E' = \frac{E_2C_1 - E_1C_2}{C_1 - C_2}.$$

For the relation to hold accurately, R and E must not change appreciably during the short period from the change of current to the reading of the new amperage and voltage, and our observations showed that the change was small unless there is a very rapid change at the instant the current is altered, followed by the slow change observed on the instrument.

On isolating the cell for the measurement of E_a, the needle of the voltmeter was found to swing rapidly down, pause at a certain voltage, which could be easily read, and continue to swing downward at a very much slower rate. The voltage at the pause was taken as E_a. Here, again, unless there was an extremely rapid fall of the reversible *e.m.f.* followed by the much slower fall observed on the instruments after the pause, it must be conceded that E_a represents the back *e.m.f.*, and in any case it is a figure of some significance, because it is reproducible: the same figure being obtained on repetition, even if the rate of fall after the pause is greater than before (a result of less perfect insulation of the electrodes).

The cell on which the measurements were made had a smooth platinum anode and wrought iron cathode. It was not possible to measure its "static" resistance, that is, the resistance with no direct current passing, but it has been calculated approximately from the cell dimensions and the solution resistances.

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Experimental Results.

A large number of measurements were made, but only a few representative figures are quoted here.

(1) Chlorate cell; variation with temperature.*

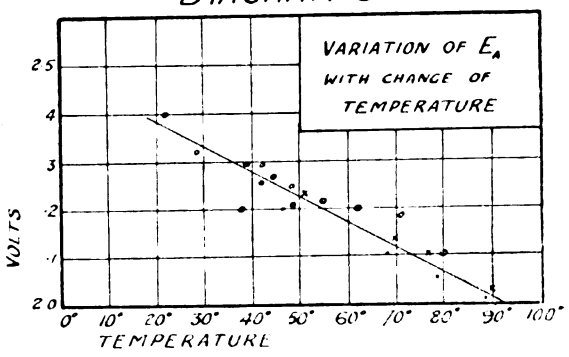
C = Current density in amps. per sq. decimetre.

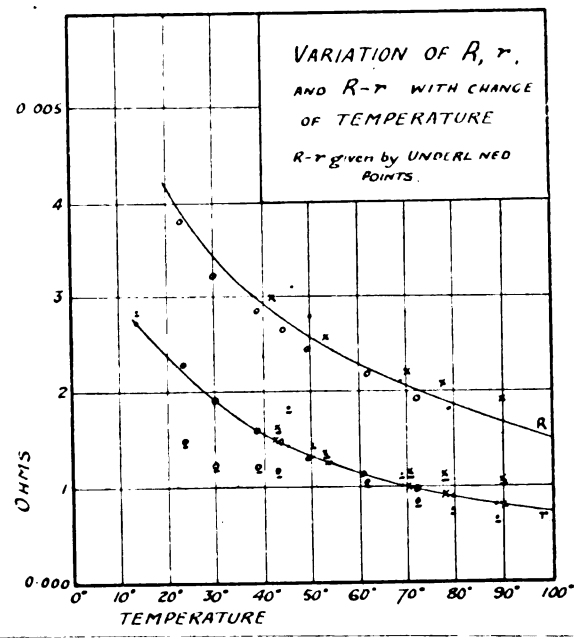
r = Approximate "static" resistance.

T	C	E_a	E_b	R	r	R − r
13.5°	35	2.31	1.07	0.0055	0.0027	0.0028
47°	38	2.20	0.89	0.0031	0.0014	0.0017
69°	38	2.10	0.83	0.0021	0.0010	0.0011
90°	39	2.00	0.71	0.0014	0.0008	0.0006

Composition of solution NaCl: 121 g/l, $NaClO_3$: 460 g/l, $NaClO_4$: 30 g/l.

DIAGRAM C





* The cell was fitted with a steam coil to enable the temperature to be controlled independently of the current density.

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(2) Chlorate cell; effect of current density.

T	C	E_a	E_b	R	r	$R-r$
80°	38	2.10	0.93	0.0019	0.0009	0.0010
80°	24	2.10	0.90	0.0020	0.0009	0.0011
80°	41	2.10	0.91	0.0020	0.0009	0.0011
80°	23	2.10	0.93	0.0020	0.0009	0.0011

Other measures were confirmatory of the inappreciable effect of variation within these limits.

The general deductions from all the measurements made are as follows:—

(1) The magnitude of E_a depends upon the temperature and the electrolyte composition (in the chlorate cells, especially with regard to hypochlorite content). It is unaffected by change of current density within fairly wide limits. Its variation with temperature would appear to be approximately linear between 20° and 90°, and it is reflected in diagram C, the rate of change being approximately 0.0054 volt per ° C.

(2) E_b appears to decrease with increase of temperature, but the variation is very irregular. It is considerably greater in the perchlorate than the chlorate cells, even for the same temperatures, but varies considerably in different cells of the same series.

(3) The variation of R, r, and $R-r$ is shown on diagram C. $R-r$ does not appear to be appreciably affected by change of current density, but in a perchlorate cell it is dependent upon the stage of the conversion, and increases considerably towards the end. The total resistance of a perchlorate cell is thus much higher at the end than at the beginning, although the liquor resistance may be the same.

At present no explanation is offered as to the exact nature of the *e.m.fs.* and resistances that have been measured, but it may be remarked that it appears difficult to account for the whole of the *e.m.f.* of the cell by applying the values for overvoltage* and transfer resistance† which have been given by Newbery. His measurements were not made in the same solutions, but the difference found would hardly be expected.

PART II.—CHLORATE FORMATION.

By N. V. S. Knibbs.

The theory of the formation of chlorate by electrolysis which is generally accepted is due mainly to Foerster and Müller. When a solution of sodium chloride is electrolysed in a cell in which the two electrodes are close together, sodium hypochlorite is formed. It results from the liberation of chlorine at the anode, and its reaction with hydroxyl ions to form hypochlorous acid,

$$Cl_2 + OH' = HOCl + Cl'$$

and a solution of chloride will at first evolve chlorine until there is a sufficient concentration of hydroxyl ions present to enable this

* Newbery, *J. Chem. Soc.* *112*, 1066, 1107 (1916).

† Newbery, *Trans. Farad. Soc.* *15*, 126 (1919).

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reaction to proceed at the necessary velocity. The hypochlorite concentration will continue to increase until other reactions, electrochemical or chemical, which decompose it, have increased to such an extent that the rate of decomposition is equal to the rate of formation by the current. The decomposition of the hypochlorite is attributed mainly to (1) Discharge of hypochlorite ions at the anode with formation of chlorate and liberation of oxygen, $6ClO + 3H_2O = 2HClO_3 + 4HCl + 3O$, and (2) Reaction of hypochlorite ions with free hypochlorous acid to form chlorate, $OCl' + 2HOCl = ClO'_3 + 2HCl$. Chlorate formation has also been attributed to other reactions, such as that between simultaneously discharged hydroxyl and hypochlorite ions.

It will be seen that, since oxygen is liberated in reaction (1), the formation of chlorate by this process is necessarily attended by loss of efficiency, and it may easily be shown that the maximum attainable is 66.6 per cent. Moreover, there is reason to believe that other reactions between the discharged hypochlorite ion and water take place which result in the liberation of an even larger quantity of oxygen, and that these reactions predominate at elevated temperatures. The second reaction, on the other hand, is purely chemical, and involves no loss of oxygen, and therefore no loss of efficiency. On this account it is the one selected for the production of chlorate technically.

It is clear from the equation representing reaction (2), that the velocity will depend upon the concentration of free hypochlorous acid present in the solution, and it is generally stated that the latter is kept acidic by the addition of an acid or acid salt. Actually, however, neutral chloride solution evolves chlorine until slightly alkaline, on the passage of any but a very low current—alkalinity being necessary in order that the reaction of the chlorine with hydroxyl ions may take place with sufficient velocity. But, although alkaline, it is still possible to have a sufficient concentration of free hypochlorous acid present, owing to the weakness of the acid, which has an ionisation coefficient (3.7×10^{-8})* less than that of carbonic acid. Since it is possible to produce solutions of hypochlorite containing 44 g/l with a current efficiency of about 87 per cent.,† the initial efficiency of the conversion being nearly 100 per cent., it might be concluded that the production of chlorate, in which the hypochlorite is continuously being converted by a purely chemical reaction, could be carried out at an efficiency of nearly 100 per cent. It is well known in technical practice that so high a current efficiency is not attained, but in the literature of the subject it does not seem to have been clearly pointed out wherein lies the cause of the loss of efficiency.

In any process of anodic fixation of oxygen, loss of efficiency may be due to two causes, namely: (1) Free oxygen may be evolved. (2) A proportion of the oxidised product may be reduced at the cathode by hydrogen. The efficiency of the formation of any given oxidised product may also be reduced by the formation of a more highly oxidised substance (*e.g.*, chlorate, when hypochlorite is required). The cathodic reduction of hydrogen may be nearly entirely prevented

* Sand, *Zeit. Physikal Chem.* *48*, 610 (1904).

† See, for instance, Allmand, *Principles of Applied Electro-Chemistry*, p. 328.

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by the presence of certain compounds in the electrolyte, that most frequently employed being a soluble dichromate. Its influence is ascribed to the formation on the cathode of a thin diaphragm of insoluble chromium chromate, produced by the reduction of dichromate to chromic ions. The diaphragm is said to prevent contact of the bulk of the solution with the electrode, and thus with the nascent hydrogen.* Accurate measurements on the extent of the cathodic reduction in the chlorate cells were not completed, but all that was done pointed to its being unimportant compared with other sources of loss of efficiency.

Anodic oxygen evolution may be due to (1) discharge of hydroxyl ions; (2) discharge of chlorate ions, and (3) discharge of hypochlorite ions. The electrolytic potential of hydroxyl ions is much lower than that of chloride or chlorate ions, but the overvoltage of oxygen is high, and this is said to raise the discharge potential to a figure above that of chloride ions. On this supposition hydroxyl ions would be discharged in amount only sufficient to maintain the overvoltage, and if other ions which liberated oxygen were being discharged, it is conceivable that no hydroxyl ions at all would be liberated. Probably a factor of more importance is the minute concentration of oxygen and hydroxyl ions present, together with the high current density which is used.

Chlorate ions have a higher discharge potential than the chloride ions, so that the latter will be discharged first, and as long as there is a sufficient concentration of them, there will be little discharge of the chlorate ion. Discharge of ClO may result in either evolution of oxygen or formation of perchlorate. The latter is formed to a slight extent in the chlorate cell, showing that a certain amount of ClO'_3 discharge does take place, but all the evidence points to its being small.

There remains, then, hypochlorite ion discharge as a source of loss of efficiency. The reaction occurring after discharge may conceivably take place in a number of ways, *e.g.* (1) $6ClO + 3H_2 = O\ 2HClO_3 + 4HCl + 3O$, as proposed and supported by Foerster,

(2) $2ClO + H_2O = 2HOCl + O$, as proposed by Oettel,

(3) $6ClO + 3H_2O = 3HClO_3 + 3HCl$.

There seems to be no evidence that reaction (3) takes place to an appreciable extent, but at elevated temperatures it would appear that reaction (2) predominated, because with high hypochlorite content oxygen is evolved in amount far more than would correspond to reaction (1).

The potential for ClO discharge has not been determined with any accuracy, but there can be no doubt that hypochlorite ions are discharged at a potential lower than that at which chloride ion discharge takes place. This being the case, these ions would be discharged to the exclusion of all others if there were a sufficient concentration of them; but working at high current densities, it is to be expected that at low concentrations there would not be a sufficient number in the neighbourhood of the anode to carry all the current,

* Müller, *Zeit. Electrochem.* 5, 469 (1899); 7, 398 (1901); 8, 909 (1902). Müller showed, for instance, that at mercury, where no coherent film could be produced, the presence of chromate did not prevent reduction.

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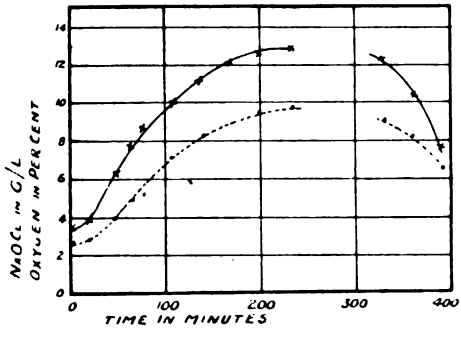
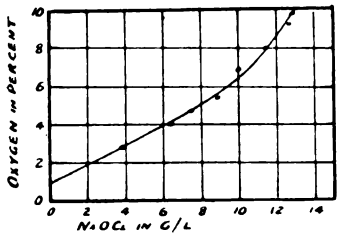
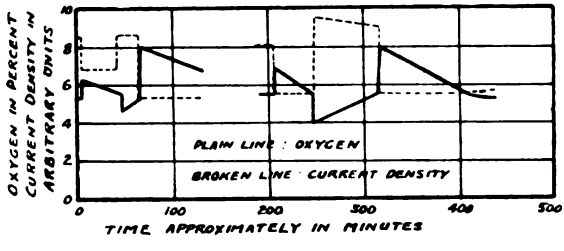
and hence chloride ions, which are in large excess, would be discharged. It would further be expected that, if OCl' ions are in such concentration that their discharge accounts for only a small fraction of the total current, the number discharged would be approximately proportional to the hypochlorite concentration. A considerable amount of evidence was obtained on these points, and the results of one experiment are given below.

DIAGRAM D



CURVES SHOWING INCREASE OF HYPOCHLORITE IN, AND OXYGEN EVOLVED FROM, A CHLORATE CELL





VARIATION OF OXYGEN WITH CHANGE OF CURRENT

A digression may here be made to indicate the use of the analysis of the gas evolved from the cells in the investigation of the efficiency of the process. Owing to the proximity of the electrodes to one another, the gases from anode and cathode of a chlorate cell are mixed before they emerge from the electrolyte, and if it is assumed

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that no oxidation of the hydrogen has taken place—an assumption which normally will lead to minor error only—the oxygen in the mixture will be a measure of the loss of efficiency. It is easy to show that if A is the percentage of oxygen in the gas, the current efficiency is (100—3A)/(100—A). These gases, being a mixture of pure hydrogen and oxygen, are susceptible to very easy analysis, and an apparatus was devised by means of which a determination could be carried out in about one minute.

In order to determine whether oxygen evolution was due to hypochlorite ion discharge alone or to hypochlorite and hydroxyl or other ions together, a chlorate cell, running normally, was selected, and sodium hydroxide solution added to suppress the hypochlorous acid. If the oxygen evolution were due to hydroxyl ions to an appreciable extent, it would be expected to increase immediately after the addition of the alkali, whereas if it be due mainly to hypochlorite its increase would follow that of the hypochlorite content. The experimental results are illustrated in diagram D, and from them it is concluded that oxygen evolution is due mainly to OCl' discharge. It is seen that oxygen evolution at first increases in direct proportion to the increase of hypochlorite content, and later at an even faster rate. The curve of increase extrapolated down to zero NaOCl cuts the oxygen axis at a little under 1 per cent., but in other experiments this point varied between 0 and 1.5 per cent., so it cannot be taken to be of much significance. On the other hand all experiments confirmed the approximately linear increase of oxygen with increase of NaOCl concentration.

Postulating that loss of efficiency is due to discharge of hypochlorite ions and at constant temperature proportional to their concentration, it is proposed now to examine the factors which determine this concentration. In the electrolytic cell, when the current is passing, there is an equilibrium set up in which the hypochlorite formed by the current is equal to that which is changed to chlorate by the reaction:—$OCl' + 2HOCl = ClO_3' + 2H^+ + 2Cl'$. For equilibrium: Hypochlorite produced per unit volume of solution by the current = Hypochlorite changed per unit volume by the reaction. The hypochlorite produced is proportional to the current C, and if the volume of the solution in the cell is v,* the NaOCl per unit volume in unit time will be $k \times Cn/v$ where k is a constant and n the current efficiency.† The amount changed per unit of volume and time depends upon the concentration of the HOCl and the temperature T, and may be represented by:—

$$k' [OCl'] \cdot [HOCl]^2 \cdot f(T)$$

where f (T) is the temperature coefficient of the reaction. For equili-

* v is the "effective" volume of the cell, and is equal to the total volume only if the latter is all subject to circulation and mixing. Any stagnant parts of the cell liquor are not to be included in the evaluation of v.

† The effect of the volume of solution and the current upon efficiency was pointed out in a paper by Müller and Koppe, *Zeit. Elektrochem. 17*, 421 (1911.) It is curious that so long a time has elapsed between Foerster's paper, in which he states his theory [*Zeit. anorg. Chem. 22*, 1 (1899)], and this observation of an effect which follows directly from the theory and which is of such importance in the design of the chlorate cell.

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brium, therefore:—

$$k.\ Cn/v = k'\,[OCl']\ .\ [HOCl]^2\, f\,(T)$$

$$\text{or } [OCl'] = K\,\frac{Cn}{v\,[HOCl]^2\, f\,(T)}$$

Experiment has shown that under given conditions of temperature and current density the loss of current efficiency (as measured by the oxygen evolution) is approximately proportional to the concentration of hypochlorite. The discharge of hypochlorite ions is limited by the number available in sufficient proximity to the electrode, and owing to the increase of mobility, the number discharged would be expected to increase with increase of temperature at a rate approximately proportional to the increase in mobility. On the other hand, the number discharged would be nearly independent of current density for all high current densities, so for a given concentration of hypochlorite the loss of efficiency and percentage of oxygen in the evolved gas would be expected to be approximately inversely proportional to the current.

Experiments were carried out to determine the effect of current density, which was varied by the same means as that employed in carrying out the *e.m.f.* measurement given in Part I. The temperature was kept at 80° by means of a steam coil in the cell. Readings of current and determinations of the oxygen in the gas evolved, and the hypochlorite in the cell liquor were made at frequent intervals. The results are shown graphically in diagram D. It will be seen that upon change of current the oxygen changes in the opposite direction, the alteration being approximately in inverse proportion. No closer agreement could be expected in an experiment of this kind. After the sudden change due to the alteration of current, the oxygen in each case tends to return to about its original value. This is due to the alteration of the hypochlorite concentration, which decreases when the current density is lowered, and increases when it is raised. A change of current density upsets the equilibrium in the cell, but when it is re-established, the percentage of oxygen is nearly the same as before, and it appears from all the experiments that, within the limits of current density used, the percentage of oxygen would be approximately independent of the current when the cell is in equilibrium, if the cell temperature were independent of the current. For a given concentration of hypochlorite, however, by this and other experiments, it has been conclusively proved that the percentage oxygen varies inversely as the current, as long as the former is small compared with the equivalent of the whole current. Since the loss of efficiency is approximately a linear function of the oxygen—the actual relation, $1 - n = 2a/(100 - a)$, approximating to that with an error no larger than the experimental errors in the above determinations—it follows that "loss of efficiency" may be substituted for "percentage of oxygen" in the above discussion.

Reliable data regarding the effect of temperature are not so easily obtained. Sudden changes of temperature, similar to the current density changes, cannot, of course, be brought about, and the conditions in the cell alter considerably during the most rapid temperature changes that it was possible to produce. The change of mobility of an ion with the temperature seems to be (very roughly) approximately proportional to the reciprocal of the change of viscosity of the

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solution. Assuming that this is so, and that the temperature coefficient of the solution is the same as that of the pure solvent, water, the alteration in the current efficiency between the temperatures (60° and 80°) at which measurements were made, would be expressed approximately by the formula:

$$(1 - n_T) = (1 - n_{80}) [1 + 0.014 (T - 80)]$$

where n_{80} is the efficiency at 80°, 0.014 being the approximate reciprocal viscosity coefficient at these temperatures. The best that can be said of the measurements that were made is that they are not inconsistent with this formula.

It is now necessary to express the current efficiency in terms of the hypochlorite concentration in the cell, and this can be done in the form*:—

$$1 - n = k_1 [OCl'] F(T) / C \dagger$$

$$\text{or } [OCl'] = k'' \frac{1 - n}{F(T)} . C$$

Hence $$k'' \frac{(1 - n) C}{F(T)} = K \frac{Cn}{v [HOCl]^2 f(T)}$$

$$\therefore \quad 1 - n = \frac{K F(T)}{k''. v. [HOCl]^2. f(T) + K.F(T)}$$

or, putting K in its original form ($K = k/k'$)

$$1 - n = \frac{k. F(T)}{k k''. v [HOCl]^2. f(T) + k. F(T)}$$

To apply this expression the values of the constants k, k' and k'' and the forms of the functions f (T) and F (T) are required. In what follows the minute is taken as the unit of time.

k'' is equal to $1/k_1$ in the expression $1 - n = k_1 [OCl'] F(T)/C$, and at 80° the average of a number of measurements of oxygen and hypochlorite at different current densities came out at $k = 0.00045$. It has also been shown that between 60° and 80° it is probable that F (T) may be approximately represented by the expression [1 + 0.014 (T—80)]. k is the constant in the relation: NaOCl produced by the current = kCn. Now one ampere-minute at 100 per cent. efficiency produces 0.000311 gram-ion of OCl, therefore $k = 0.000311$. k' and f (T) both occur in the relation: NaOCl changed to chlorate per minute = $k' [OCl'] [HOCl]^2 f(T)$, and in Part I it was found that between 60° and 80° $k f(T)$ could be expressed by the formula: $e^{0.60 + 0.056T}$.

* The hypochlorite ion discharge will also depend upon the concentration of chloride in the solution, but if this is always high compared with the hypochlorite, any change in the concentration will alter very little the hypochlorite ion discharge.

† C should really be measured as a current density in amps. per square decimetre of electrode, but in order that it may cancel with the C in the other expression (without introducing another constant) we leave it as the total amperage passing through the cell. The constant k'' consequently applies only to a cell of the same anode area as that on which the measurements were made. For any other area of anode we have :— $k''_1 = k'' \times 23/\text{anode area in sq. decimetres.}$

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Substituting these values for the constants:

$$1 - n = \frac{0.000311\ [1 + 0.014\ (T - 80)]}{0.00045\ v\ [HOCl]^{\frac{1}{2}}\ e^{0.60 + 0.056T} + 0.000311\ [1 + 0.014\ (T-80)]}$$

for temperature between 60° and 80°.

The numerator and denominator may conveniently be multiplied by one million. It is evident that the efficiency will increase with increase of v and [HOCl], whilst T acts in both directions.

In applying the formula the difficulty of the accurate determination of the hypochlorous acids presents itself, but, taking the best values obtained, the efficiency figure in most cases agreed well with that calculated from the oxygen evolved, and large differences were usually traceable to the cell not being in equilibrium. The agreement is satisfactory, considering the approximations that have been made.

In the foregoing the current efficiency of the process has been dealt with, no account being taken of the voltage of the cell. It is now proposed to investigate the total energy efficiency of a chlorate cell. Foerster and Muller* found that a 95 per cent. current efficiency at 2.4 volts could be obtained in the preparation of chlorate by using a very low current density and high HOCl concentration, but under technical conditions a much higher voltage is required. To calculate the percentage energy efficiency a value must be assumed for the voltage theoretically required to bring about the formation of chlorate, but the figure to take is by no means obvious, and none that has been proposed seems to have very much significance. According to Luther, 1.43 volts is the theoretical voltage required to produce chlorate from chloride, but the voltage corresponding to the thermal absorption in the change:—

NaCl. Aq. + $3H_2O$(Liquid) = $NaClO_3$ Aq. + $3H_2$(gas) − x cals. is 1.62 volts (since x = 224,000 cal.).

The factors which determine the current that is produced in a cell by a fixed voltage applied to the electrodes are:—(1) The resistance of the solution in the cell; (2) any other resistance (*e.g.*, "transfer" resistances at the electrodes); (3) the voltage required to reversibly discharge the ions; (4) the additional voltage required at the electrode for continuous discharge at the required rate (overvoltage). Each of these factors is dependent upon the temperature, and probably also, but in general to a much lesser extent, upon the liquor composition. The transfer resistances and overvoltage also depend upon the nature of the electrode surfaces. Assuming, however, constant conditions with regard to liquor composition and electrode surfaces, the factors may all be expressed as functions of the temperature. If the cell is heated by no means other than the passage of the current,† the temperature is itself a function of the current and voltage, so that it should be possible to express the current in terms of the voltage applied to the cell, for a given composition of cell solution. The determination of the constants in the complete thermal equation of the cell is rather a complicated undertaking, and there was not time to complete the investigation.

The energy of the current passing through the cell is given by the product EC, and in one minute it is equivalent to 14.34 EC

* *Zeit. Elektrochem.* *8*. 8 (190[illegible]).

† This is the case, we believe, with all technical cells.

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calories. A portion of this is used in the chemical reactions in the cell, and the remainder is lost by radiation, etc., and as latent heat in the water vapour carried off from the cell. If all loss of efficiency is due to oxygen evolution, the heat used in the chemical reactions in the cell at about 70° is 0.000104 C(n × 17,000 + 3 × 68,000).

The heat lost by radiation, convection, etc., is apparently of less importance than the loss as latent heat in the water vapour, and the thermal insulation of the cells results in only a slight increase of temperature.

During electrolysis the hypochlorous acid concentration in the solution decreases, owing to its volatility. The loss increases with increase of temperature, and this is a consideration in deciding upon the temperature to be maintained in the cell. In any case the loss has to be made good, and there has been a number of methods proposed for accomplishing this. Amongst them are (1) the continuous addition of a very weak acid, *e.g.*, carbonic acid, by bubbling a slow stream of carbon dioxide through the solution; (2) the addition at intervals of the salt of a strong acid with a weak base, with a view to the continuous renewal of the hypochlorous acid by the hydrolysis of the salt; (3) the addition of a strong acid or acid salt, *e.g.*, hydrochloric acid or potassium hydrogen fluoride. It was found that the regulated addition of hydrochloric acid was the most satisfactory of all the methods which were tried. Carbon dioxide probably gives good results, but for technical use it is not very satisfactory. The use of an easily hydrolysable salt would be excellent if one could be found with the correct properties, but a careful trial of certain hydrolysable chlorides, which have been recommended for this purpose, failed to show any superiority in maintaining hypochlorous acid concentration over the equivalent amount of hydrochloric acid.

Insoluble impurity in the electrolyte increases the resistance of the solution, and therefore the cell voltage. It also has the effect of reducing the current efficiency of the cell by facilitating the loss of hypochlorous acid from the solution. A further deleterious effect is its erosive action on the electrodes—a feature of special imporance when platinum anodes are used.

The conductivity data given in Part I permit the determination of the solution composition which will give the lowest voltage drop in the solution. They indicate that the higher the proportion of chloride to chlorate, the better is the conductivity, but the subsequent separation of chlorate from the solution renders it necessary to maintain a high concentration of this salt, and in consequence optimum conditions with regard to conductivity cannot be attained.

Summary.

(1) The generally accepted theory of chlorate formation is set out.

(2) The sources of loss of efficiency are discussed, and the conclusion is arrived at that normally it is due mainly to hypochlorite ion discharge.

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(3) An equation is developed to express the efficiency in terms of temperature and the other controlling factors. It takes the form:—

$$1 - n = \frac{k\ F\ (T)}{k'\ k''\ v\ [HOCl]^2 f\ (T) + k\ F\ (T)}$$

(4) Experiments to obtain the constants of the equation are described, and with these substituted it becomes:—

$$1 - n = \frac{311\ [1 + 0.014(T-80)]}{450v\ [HOCl]^2\ e^{0.60\ +\ 0.56T} + 311\ [1 + 0.014\ (T - 80)]}$$

for temperatures above 60°.

(5) The energy efficiency of the chlorate cell is discussed.

(6) Brief reference is made to the methods of maintaining hypochlorous acid concentration, and to the effect of insoluble impurity in a cell.

PART III.—PERCHLORATE FORMATION.

By N. V. S. KNIBBS.

The theory of the mechanism of the electrolytic formation of perchlorate from chlorate, which seems to have been fairly generally accepted, is that due to Oechsli.* Recently it has been criticised by Bennett and Mack,† who offer an entirely different explanation of the observed facts; a theory which was evolved from the new theory of overvoltage proposed by Bennett and Thompson.‡

Oechsli's theory may be expressed briefly as follows:—Chlorate ions are discharged at the anode, and there react with water, forming chloric acid and oxygen: $2\ ClO_3 + H_2O = 2HClO_3 + O$. The free chloric acid is at high concentration in the film of electrolyte in immediate contact with the anode, and under these conditions spontanous decomposition takes place with the formation of perchloric and chlorous acids—

$$2\ HClO_3 = HClO_4 + HClO_2.$$

The chlorous acid is immediately oxidised by the nascent oxygen formed by the reaction of the discharged chlorate ions with water, with the result that this oxygen is not liberated as a gas. The relative efficiencies at smooth and rough platinum, and the effect of alkalinity, current density, temperature, and time upon the efficiency was held to support the theory.

Bennett and Mack point out that there is no direct evidence that chloric acid decomposes in the manner assumed, the evidence pointing rather to a different reaction. They also do not think that Oechsli's theory explains the temperature effect and the result of platinising the electrode. Their theory is that perchlorate formation is due to the direct addition of oxygen to the chlorate ion, the latter not being discharged at the anode, but oxidised in its vicinity by active oxygen, O_1, produced there. Schoch's experiments,§ in which perchlorate formation began at an anode potential of + 0.023

* *Zeit. Elektrochem.* 9, 807 (1903).
† *J. Am. Electrochem. Soc.* 29, 323 (1916).
‡ *Ibid.*, p. 269.
§ *J. Phys. Chem.* 14, 669, 735.

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volts, whilst oxygen was not evolved until + 1.5 volts, are quoted to prove that perchlorate formation is not determined by chlorate ion liberation, since its discharge potential is much above 0.023 volt, and it is concluded that the oxidation of chlorate demands a lower potential than the evolution of oxygen. Previous to Bennett and Mack's paper, it was generally believed that chlorate in solution was not directly oxidisable to perchlorate, but by a series of experiments these authors showed that in acid solution oxidation could be effected by several reagents, persulphate being the most effective.

An examination of Bennett and Mack's paper leads to the conclusion that their objections to the theory of chlorate ion discharge cannot be upheld. The effect of platinising the anode is due, not merely to the decreased current density, as they assume, but to the decrease of oxygen overvoltage, which facilitates hydroxyl ion discharge, and hence decreases the efficiency. According to the active oxygen theory, the formation of molecular from active oxygen is catalysed by the platinised surface, that is, the oxygen overvoltage is reduced, so that the observed phenomena are explained as well by one hypothesis as by the other. The effect of temperature is due to increase of hydroxyl ions, decrease of overvoltage, and increase of mobility of the hydroxyl ions, not, as assumed, merely to the first of these three factors. On the active oxygen theory the decrease in efficiency with rise of temperature should follow the decrease of overvoltage, and this is not the case. The formation of perchlorate observed by Schoch may be due to the " residual " discharge of chlorate ions. An insurmountable objection to Oechsli's theory—but not to the chlorate ion discharge hypothesis—is that in the case observed by Schoch it is impossible to conceive that a sufficient concentration of chloric acid was produced to bring about the supposed decomposition. Another objection is that any diffusion of chloric or chlorous acids away from the anode would result in loss of efficiency, and it is difficult to believe this diffusion to be so small in the highly agitated technical cells, that efficiencies of 98-99 per cent. could be attained.

The active oxygen theory does not satisfactorily explain the effect of alkalinity on efficiency, and though the direct oxidation of chlorate by persulphate was definitely proved, the evidence with other reagents seems rather inconclusive. For instance, oxygen activated by ultra-violet light oxidises the chlorate to the extent of 1 per cent. only, no further oxidation being effected by continued action. This is very difficult to understand, unless the reaction be reversible, and it cannot be reversible, because perchlorate is not a source of active oxygen. However, a more definite criterion for testing the active oxygen theory is available. The active oxygen produced at the anode is used up in the two reactions:

$$2O_1 = O_2 \qquad (1)$$
$$O_1 + ClO_3' = ClO_4' \qquad (2)$$

The former results in gaseous oxygen liberation and loss of efficiency, the latter in perchlorate formation. During the electrolysis of a chlorate solution the concentration of active oxygen on the anode will be such as to make the velocities of the two reactions just sufficient to account for all the oxygen discharged. Now, if the current be increased, the active oxygen will increase until the two velocities

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have risen sufficiently to balance the extra oxygen discharged. Since reaction (1) is proportional to the square of the concentration of active oxygen, it will increase to a greater extent than reaction (2), that is, the efficiency of perchlorate formation will decrease. Actually the efficiency increases with increase of current.

It will have been observed that the legitimate objections to Oechsli's theory are applicable only to the reactions supposed to take place after discharge of the chlorate ion. The mechanism which he proposed would appear to be unnecessarily complicated, and the similarity of the effects of temperature, current density, etc., on perchlorate and persulphate formation suggests a similiarity of mechanism.* Perchlorate formation may take place as follows:—

$$O_2\ ClO— + —OClO_2 = O_2Cl—O—O—ClO_2 \quad (1)$$

$$O_2\ Cl—O—O—ClO_2 + HOH = O_2Cl—O—O—H + O_2ClOH \quad (2)$$

$$O_2\ Cl—O—O—H = O_2Cl\ OH. \quad (3)$$

Reaction (1) is analogous to the formation of persulphuric acid, $O_2(OH)S—O—O—S(OH)O_2$, but a peroxide is formed which is naturally acted upon by water according to reaction (2). Reaction (3) is a rearrangement to a more stable form: a result of the higher valency which chlorine is capable of assuming. It is believed that this mechanism is not open to the objections which may be advanced against Oechsli's theory, and that it is in harmony with the observed phenomena.

Perchlorate formation, on the above hypothesis, depends upon the discharge of chlorate ions at the anode, and any other anodic discharge will result in loss of efficiency. The other anions present are hydroxyl, chloride, hypochlorite and perchlorate, the chloride as an impurity in technical chlorate, and the hypochlorite as a result of its electrolysis. Except perchlorate, all those ions are discharged at a lower anodic potential than chlorate, but, as in the case of the chlorate cell, their relatively small concentration limits the proportion of the total current which their discharge is able to transfer at any but low current densities. The effects of current density and temperature upon current efficiency have been ascribed to the effect of these factors upon overvoltage and of the latter factor upon the ionisation of water, but from our observations it would appear that under technical conditions these are not the predominating agents.

As in the chlorate cells, hydroxyl ion discharge appears to play a small but definite part in the efficiency loss, and if all other losses were eliminated, there would still be a small oxygen evolution due to this factor. Normally it is very small, but the anodic potential in these cells is considerably higher than in the chlorate cells, and on this account oxygen evolution in the former increases at a faster rate with increase of alkalinity.

The presence of chloride in the perchlorate cell solution and its effect upon efficiency does not appear to have received much attention in the scanty literature of the subject. All technical chlorate contains some chloride as impurity, and it is evident that chlorate made by the usual electrolytic method may contain up to one or two per cent., unless it is purified by recrystallisation. Even if pure

* The fact that persulphate alone, of all the oxidising agents tried, oxidised chlorate strongly, perhaps lends additional support.

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chlorate is used in making up the solution for electrolysis, the latter will be found to contain chloride after the current has passed for a few hours, due to certain reactions which are referred to again below.

This chloride is discharged at the anode, and forms hypochlorite, which in turn is discharged with evolution of oxygen. The hypochlorite formed will depend upon the concentration of chloride, and therefore, for a given temperature and hypochlorous acid concentration, the loss of efficiency will depend upon the chloride. The hypochlorous acid concentration is limited by the hydroxyl ion required to react with the chlorine liberated at the anode* and any acidity of the solution results in chlorine evolution.† Unless acid is added to the cell at very frequent intervals, the reaction hypochlorite to chlorate is very slow at temperatures up to 60° C.‡

The higher the temperature at which it is possible to work, the lower will be the hypochlorite relative to the chloride, but the temperature is limited by several considerations. In the first place, it is stated that perchlorate formation tends to become zero at about 80°—90° and the curves given by Winteler§ support this assertion. From a study of these curves it would appear that a very low temperature is necessary for good current efficiency, and 10° has been quoted as that worked to in technical practice. With high current density so low a temperature is quite unnecessary, and high efficiency is possible at 60° and over. Nevertheless, it appears probable that at high temperature the discharge of chlorate ion does not result in perchlorate formation exclusively, the reaction being accompanied by others which involve oxygen evolution, such as the formation of chloric acid in the ordinary manner ($2ClO_3 + H_2O = 2HClO_3 + O$). The relative amounts contributing to perchlorate formation and oxygen evolution would depend upon the temperature and current density, but above 30 amps. per square dm. oxygen evolution from this cause is probably negligible up to about 65°—70°.

High temperature tends to increase the loss of efficiency due to hypochlorite and hydroxyl ion discharge, owing to increased mobility, but against this is to be set the decrease of hypochlorite due to the increase in the velocity of its conversion, and if it were not for another effect of temperature referred to below, it would be possible to work at 60° or over and still maintain high current efficiency. This is shown by the following experiments carried out on a perchlorate cell running normally.

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* At the lower temperatures of the perchlorate cells a higher hydroxyl ion concentration is required, presumably owing to the lower velocity of the reaction and to the shifting of the equilibrium of the reaction $Cl_2 + OH' = Cl' + HOCl$ to the left with decrease of temperature.

† When a neutral chlorate solution containing chloride as impurity is first put in circuit chlorine is liberated as in the case of a chloride solution, the amount evolved depending upon the amount of chloride present. The greater the chloride concentration, the more chloride ions there would be liberated at the anode, and hence the greater hydroxyl concentration required.

‡ Chlorate formation by discharge of hypochlorite ions and reaction according to the equation: $6\,ClO + 3H_2O = 2HClO_3 + 4HCl + 1\frac{1}{2}O_2$, is probably not negligible at the temperatures of the perchlorate cells.

§ *Zeit. Elektrochem.* 7, 635 (1901).

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(1) Chlorate: about 470 g/l.
Current density: about 36 amps./sq. dcm.

Time ...	11 a.m.	1.30 p.m.	3.30 p.m.	5.0 p.m.
Temp. ...	34°	50°	60°	66°
Oxygen % ...	0.4	1.0	1.4	2.0
Efficiency % *	99.2	98.0	97.2	95.9

(2) Chlorate: about 130 g/l.
Current density: about 38 amps./sq. dcm.

Time ...	11.30 a.m.	1.30 p.m.	5.0 p.m.
Temp. ...	50°	60°	73°
Oxygen % ...	0.8	1.3	2.6
Efficiency %* ...	98.4	97.4	94.7

It should be noted that each experiment occupied only 6 hours, and that the cell was maintained at the higher temperatures for a fraction only of this time.

The other effect mentioned is the dependence of the chloride content of the cell upon the temperature. In the electrolysis of a chlorate solution, chloride is formed, and its concentration increases until the rate of its conversion to chlorate through hypochlorite is equal to that of its formation. Chloride may conceivably be formed either at the cathode by reduction of the chlorate by hydrogen, or at the anode as the result of a side reaction, possibly that represented by the equation: $4\ HClO_3 = 3\ HClO_4 + HCl$. It is found that the presence of chromate reduces the amount of chloride in equilibrium at any temperature, a fact which favours the theory that the chloride is formed by hydrogen reduction. On the other hand, chloride is formed to a considerable extent even in the presence of chromate, whereas it was found in the laboratory (using, of course, a very much lower current density) that reduction of chlorate is apparently entirely prevented by chromate. The effect of chromate in reducing the equilibrium chloride concentration is perhaps to be attributed to its prevention of hypochlorite reduction at the cathode, and the promotion of the reaction of hypochlorite to chlorate by its regulation of the hypochlorous acid. The investigation of the above effect was not completed, and it is impossible to state definitely to which reaction chloride formation is due, nor were sufficient data obtained to determine the temperature coefficient, but the following experiment affords some indication of its magnitude.

Initial solution in cell contained 2.26 g/l NaCl (and about 600 g/l $NaClO_3$).

The cell was put in circuit, and maintained at 30°—35°.

After 10 hours ...	NaCl = 2.50 g/l
,, 13 ,, ...	,, = 2.31 ,,
,, 19 ,, ...	,, = 2.29 ,,
,, 25 ,, ...	,, = 2.29 ,,
Temperature raised to 45°.	
After 31 hours ...	NaCl = 2.98 g/l
Temperature raised to 53°.	
After 37 hours ...	NaCl = 3.86 g/l†

* Calculated from the percentage oxygen.

† Equilibrium had evidently not been reached, and it would appear from the next determination that the value at 53° would probably be greater than 4.1 g/l.

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Temperature after 40 hours reduced to 28°.

After 43 hours	...	NaCl=4.08 g/l
,, 60 ,,	...	,, =2.14 ,,

To attain equilibrium a cell must be maintained for several hours at constant temperature, and the effect of an increase of temperature on the efficiency is not complete until this time has elapsed. The first effect of raising the temperature is to increase the oxygen evolution by an amount which is approximately reflected in the two experiments quoted above.* Following this immediate increase is another slower one, which follows the increase of chloride (and hypochlorite) until equilibrium is reached.

The variation of the efficiency with change of current density was determined by experiments similar to that carried out on a chlorate cell. It was found, as in the case of chlorate, that the percentage of oxygen evolved was approximately inversely proportional to the current density within the limits which obtained, but that it remained approximately constant at the new density. With chlorate formation it was found that the oxygen tended to return to a value which was the same for all current densities when the cell reached a condition of equilibrium, this being due to the altered rate of formation of hypochlorite. The final expression for the current efficiency of chlorate formation did not involve current density. In the case of perchlorate, however, the oxygen evolution is due to constituents whose concentration is not determined by the current density. Although in normal working the oxygen evolution is largely due to hypochlorite ion discharge, the hypochlorite is determined by the chloride concentration and not by the current, because the former is always small, and at all ordinary current densities the number of chloride ions discharged (forming hypochlorite) is determined merely by the number in sufficiently close proximity to the electrode. As already demonstrated, the chloride concentration is mainly dependent upon the temperature.

The usual method of production of sodium perchlorate differs from that of chlorate in that the chloride in the latter case varies only between comparatively narrow limits, and is always high in concentration, whilst in perchlorate production a solution of chlorate is almost completely converted into perchlorate. The point to which it is necessary to carry the conversion will influence very considerably the efficiency of the whole conversion, for it is obvious that when the chlorate is reduced to a concentration approaching that of the chloride, the efficiency will decrease considerably, owing to the discharge of the latter figuring to a much greater extent in the total anodic discharge. If it is necessary to reduce the chlorate to below about 10 g/l it is found that the best efficiency for the conversion of the last few grams per litre is obtained by using a moderate current density and low temperature; temperature at this stage having a much greater effect than when more chlorate is present. Under these conditions nearly all the chloride present is converted into perchlorate with moderate efficiency. It appears that in this case the hypochlorite formed is converted into chlorate by the reaction of the discharged ions and with liberation of oxygen, and an in-

* The temperature changes, however, were very far from being instantaneous, so the effect due to change of chloride was not eliminated.

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crease of the temperature probably results in a decrease of this reaction without a corresponding increase in chlorate formation by reaction of HOCl. Too high a current density decreases the efficiency owing to the discharge of perchlorate ions.

The influence of the hypochlorous acid concentration on the efficiency of perchlorate formation is dependent upon the temperature. At low temperatures it is negligible because under these circumstances the rate of chloride formation is low, and the conversion of chloride to chlorate is probably through the discharge of hypochlorite ion, and hence independent of the HOCl concentration. This has been proved experimentally, for it was found that the frequent addition of acid to a cell at 60° resulted in a considerably better efficiency than when no acid was added, but at 30° there was no appreciable effect. The addition of chromate also has a marked effect in improving the efficiency at high temperature, but here again the effect becomes inappreciable below about 35° owing to the much lesser formation of chloride.

The heat absorbed in the production of perchlorate from chlorate by the process: $NaClO_3$ Aq. + H_2O = $NaClO_4$ Aq. + H_2 (gas) is 51,400 cals., and the voltage corresponding to this figure is 1.11. In practice it is necessary to use a higher voltage than in the chlorate cells, due to the lower temperature at which it is necessary to work.* The experimental determinations of E_a, E_b and R in a perchlorate cell which were made were not sufficiently comprehensive to enable one to generalise, but from a large number of measurements the average total voltage of a cell at 30° and 40 amps. per square dcm. is found to be 6.4 volts,† and the temperature coefficient − 0.04 volts per degree above 30°. Up to the point at which the percentage decrease in current efficiency is equal to the percentage decrease of voltage an increase in temperature will increase the energy efficiency of the process. If it is unnecessary to carry the conversion of the chlorate below about 50 g/l, the best energy efficiency will result from the maintenance of a temperature of 60°—65°, but at this temperature the chloride formed causes a very low current efficiency if the conversion is carried nearly to completion. Under most circumstances the best total efficiency is obtained by varying the temperature to suit the stage of the conversion. The following experiment, one of a number carried out in the investigation of the temperature effect, is illustrative:—

Two perchlorate cells, A and B, were maintained at different temperatures throughout the conversion. The following are the data relating to them:—

Cell.	Temp.	Chlorate g/l Initial.	Final.	Current Efficiency.	Average Voltage.	$NaClO_4$ production in Grams per Watt-Hour.
A.	30°	645	4	93%	6.45	0.331
B.	60°	645	50	83%	5.26	0.392

It is seen that though the cell at 60° had a considerably lower current efficiency, its production per unit of electrical energy was greater, but the two cells were in circuit for the same time, and during this time the chlorate in A was reduced to 4 g/l, whilst in B it was

*All technical perchlorate cells have, of course, some means of cooling the solution during the electrolysis.

†Higher towards the end of the conversion.

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reduced only to 50 g/l. In this instance the conversion of B was not carried to completion,* but other experiments have shown that if it had been completed (the temperature still being maintained at 60°), the current efficiency towards the end would be so low that the energy efficiency of the whole conversion would be less in B than in A. On the other hand, if the temperature were reduced when the chlorate became low, and acid added at intervals, the final efficiency could be raised considerably, and probably the energy efficiency of B for complete conversion would be higher than that of A, though the difference between them would not be nearly as great as that reflected in the above figures.

The conductivity of chlorate and perchlorate solutions of different concentrations is given in Part I, and from the data may be selected the strength which at a given temperature has the maximum conductivity. Since the concentration with maximum conductivity is always high,† it can always be used as that of the solution in the cell. The evaporation from the cell during electrolysis will raise the concentration above the optimum point, so, in order to work throughout with a minimum voltage drop in the solution, the cell must be periodically diluted.

Summary.

(1) Oechsli's theory of perchlorate formation is given, together with the phenomena which it is held to explain. It postulates discharge of chlorate ions at the anode, followed by certain chemical reactions.

(2) Bennett and Mack's objections are referred to, and their own theory enunciated. This theory rejects chlorate ion discharge, and postulates direct oxidation of chlorate by anodic active oxygen.

(3) Both theories are discussed, and the conclusion arrived at that neither is adequate.

(4) It is maintained that perchlorate formation is due to chlorate ion discharge, but that the reactions taking place subsequently are not those proposed by Oechsli. A mechanism similar to that of persulphate formation is suggested.

(5) The factors in the current efficiency of technical perchlorate formation are then discussed, and in this connection chloride formation is shown to take place during electrolysis and to be dependent upon the temperature.

(6) The energy used in a perchlorate cell is discussed.

* When "complete conversion" is spoken of, the reduction of the chlorate to a few g/l, say 4 or less, is really meant.

† And therefore favourable from other considerations.

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Bibliography.

Kershaw—*Die elektrolytische Chloratindustrie,* Halle, 1905.

Billiter—*Die elektrochemischen Verfahren der Chemischen Gross—Industrie,* Halle, 1911.

Thompson—*Applied Electrochemistry,* New York, 1911.

Allmand—*Applied Electrochemistry,* London, 1912.

Foerster—*Elektrochemie Wässeriger Lösungen,* Leipsig, 1915.

Hale—*The Application of Electrolysis to Chemical Industry,* London, 1918.

1894-5. Oettel—Electrolytic Formation of Hypochlorites and Chlorates. *Zeit. Elektrochem. 1,* 354; *Chem. Centr. 1,* 592.

1898. Winteler—Studies on the Electrolysis of Alkali Chlorides. *Zeit. Electrochem. 5,* 10, 49, 217.

Wohlwill—Electrolysis of Alkali Chlorides. *Zeit. Elektrochem. 5,* 52.

Vaubel—Electrolytic Production of Chlorates, &c. *Chem. Zeit. 22,* 331.

Foerster—Electrolytic Preparation of Perchloric Acid and its Salts. *Zeit. Elektrochem. 4,* 386.

1899. Theory of the Electrolytic Formation of Hypochlorite and Chlorate. *Zeit. anorg. Chem. 22,* 1.

Oettel—Electrolysis of Solutions of Calcium Chloride. *Zeit. anorg. Chem. 22,* 92.

Müller—Formation of Hypochlorite and Chlorate in the Electrolysis of Alkali Chlorides. *Zeit. anorg. Chem. 22,* 33.

Electrolytic method of preparing Alkali Chlorates, Bromates, and Iodates. *Zeit. Elektrochem. 5,* 469.

Wohlwill—Electrolysis of Solution of Alkali Chlorides (Discussion). *Zeit. Elektrochem. 6,* 227, 410.

1900. Landin—Electrolytic Chlorate Manufacture (Abstract). *Zeit Elektrochem. 6,* 480.

Brochet—Electrolysis of Potassium Chloride. *Compt. rend 130,* 134, 718, 1624; *Bull. Soc. Chim. 23,* 724, 736.

Foerster & Jorre—Electrolysis of Alkali Chloride Solutions with a diaphragm. *Zeit. anorg. Chem. 23,* 158.

Foerster & Sonneborn—Evolution of Oxygen at the Anode in the Electrolysis of Alkali Chlorides. *Zeit. Elektrochem. 6,* 598.

Lorenz & Wehrlin—Electrolysis of Sodium Chloride. *Zeit. Elektrochem. 6,* 389, 408, 419, 437, 445, 461.

Wolf—Electrolysis of Sodium Chloride. *J. Phys. Chem. 4,* 200.

1901. Winteler—Studies in the Electrolysis of Alkali Chlorides. *Zeit. Elektrochem. 7,* 635.

Foerster—Transformation of Hypochlorites with Chlorates. *J. prak. Chem. 63,* 141.

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Sproesser—Electrolysis of Alkali Chlorides with Carbon Anodes. *Zeit. Elektrochem.* 7, 971, 987, 1012, 1027, 1071, 1083.

Müller—Studies in Cathodic Polarisation and Depolarisation. *Zeit. anorg. Chem.* 26, 1.

Diminution of Cathodic Depolarisation by Potassium Chromate. *Zeit. Elektrochem.* 7, 398; 8, 909.

1902. Foerster & Müller—Current and Energy Efficiencies obtainable in the Electrolytic Preparation of Alkali Hypochlorites and Chlorates. *Zeit. Elektrochem.* 8, 8.

The Behaviour of Hypochlorous acid and Hypochlorites during Electrolysis. *Zeit. Elektrochem.* 8, 633, 655.

Luther—Electromotive behaviour of Hypochlorous and Chloric Acids. *Zeit. Elektrochem.* 8, 601.

Richards—The Electrochemical Industries of Niagara Falls *Electrochem. Ind.* 1, 19.

1903. Oechsli—Electrolytic Formation of Perchlorate. *Zeit. Elektrochem.* 9, 807.

Foerster & Müller—Theory of the Electrolysis of Solutions of Alkali Chlorides. *Zeit. Elektrochem.* 9, 171.

1904. Electrolysis of Alkali Chlorides in Presence of Fluorine Compounds. *Zeit. Elektrochem.* 10, 781.

Sand—Hypochlorous Acid.—III. Formation and Decomposition of Chloric Acid. *Zeit. physikal. Chem.* 50, 465.

1905 Sirk—Acceleration of the Evolution of Chlorine from Potassium Chlorate and Hydrochloric Acid by the presence of Platinum. *Zeit. Elektrochem.* 11, 261.

Foerster & Müller—Electrolytic Formation of Chlorates (Notes on Sirk's paper). *Zeit. Elektrochem.* 11, 502.

Conlern—Chlorate Determination and the Calculation of output in the Electrolytic Chlorate Industry. *Chem. Zeit.* 29, 1072.

1907. Betts & Sherry—Experiments on the manufacture of Chlorates and Hypochlorites with a view to high current efficiency. *J. Am. Chem. Soc.* 29, 340.

1911. Müller & Koppe—Influence of Current Concentration in Electrolytic Chlorate Formation. *Zeit. Elektrochem.* 17, 421.

Anon—A New French Chlorate and Perchlorate Plant. *Met. Chem. Eng.* 10, 716.

Clarens—The Spontaneous Transformation of Hypochlorites to Chlorates and of Hypobromites to Bromates. *Compt. rend.* 157, 216.

Müller, E. & O.—The Velocity of the Chemical Formation of Chlorate determined by Electrolysis. *Festschrift* W. Nernst. 319.

1916. Bennett & Mack—Electrolytic Formation of Perchlorate. *J. Am. Electrochem. Soc.* 29, 323.

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SORPTION OF IODINE BY CARBON.

By JAMES BRIERLEY FIRTH.

(*A Paper read before* THE FARADAY SOCIETY, *Monday, June* 14, 1920, PROFESSOR ALFRED W. PORTER, F.R.S., VICE-PRESIDENT, *in the Chair.*)

Object of the Investigation.

The object of the present investigation was to study in detail the sorption of iodine by various forms of carbon; to determine as far as possible the factors which determine the sorption capacity of the carbon: in particular to study the influence of time, size of particles, and previous treatment on the sorption capacity of the carbon.

The solute throughout was iodine. The solvents employed were benzene and chloroform. The sorption agents were lampblack, sugar carbon, blood charcoal, animal charcoal, coconut charcoal from the fruit, coconut charcoal from the shell.

Formulæ.

Various formulæ have been suggested to represent sorption phenomena. The simplest formula which has been most satisfactorily used is that of the Power Law.

$$\frac{x}{m} = \beta c^{\frac{1}{p}} \quad \text{or} \quad \frac{x}{m} = \beta \left(\frac{a-x}{v}\right)^{\frac{1}{p}}$$

Where x is the amount sorbed by m grams of solid used, a is the original total amount of solute before sorption, and c is the final concentration of the solution.

The exponential is essentially an adsorption formula, and is purely empirical, devoid of theoretical basis. The formula is not valid between wide limits of concentration, but can be satisfactorily used within narrow limits.

In the present communication the Power Law will be used. For comparatively short periods the amount of *absorption* will not materially affect the utility of the equation.

The logarithmic form of $\frac{x}{m} = \beta c^{\frac{1}{p}}$ is $\log \frac{x}{m} = \log \beta + \frac{1}{p} \log c$ which is an equation for a straight line where $\frac{1}{p}$ is the slope of the line.

Since $\frac{x}{m}$ and c are determined experimentally, β and $\frac{1}{p}$ can be calculated from two sets of experiments, or β and $\frac{1}{p}$ can be determined graphically from the logarithmic diagram:

$$\left(\log \frac{x}{m}, \log c\right)$$

EXPERIMENTAL.

Materials Employed.

The *chloroform* was dried for several days over calcium chloride, then fractionated, the middle portion only being taken.

The *benzene* was fractionated several times, the first and last runnings being neglected.

The *iodine* used was Kahlbaum's, and it was resublimed before use.

With the exception of the coconut charcoals, the carbons used were supplied by Merck. The coconut charcoal, from the white tissue

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and from the shell, was prepared by carbonising at as low a temperature as possible.

Lampblack and *sugar carbon* gave less than 0.1 per cent. ash.

The *animal charcoal* as supplied gave 4.35 per cent. ash; it was digested with hot concentrated hydrochloric acid, washed with water, and finally boiled with distilled water until free from phosphates and chloride; the ash was then 0.975 per cent.

The *blood charcoal* gave an ash of 8.54 per cent. After digesting with hot concentrated hydrochloric acid, washing with water, and boiling with distilled water, the ash was 5.48 per cent.

Coconut charcoal from the fruit gave 22.49 per cent. ash. After digesting with hot concentrated hydrochloric acid, and boiling with distilled water until free from chloride, the ash was 4.9 per cent.

Coconut charcoal from the shell gave 0.93 per cent. ash, and after treatment as before, gave 0.41 per cent. ash.

Decinormal solutions of iodine in chloroform and benzene were used. The estimations were made by shaking the solutions with water in a stoppered bottle and titrating directly with sodium thiosulphate. As a rule $\frac{N}{10}$ thiosulphate solution was used, but in cases where the first experiment showed the amount of iodine to be estimated to be very small $\frac{N}{100}$, and in some cases freshly prepared $\frac{N}{1000}$, was used in repeat experiments.

Solubility of Iodine.

(a) In benzene—103.9 grams per litre at 15° C.

(b) In chloroform—36.2 grams per litre at 15° C.

The molecular formula, according to *Beckmann*, is the same in both solvents, namely I_2.

All experiments, except where otherwise stated, were carried out at 25° C. The carbon was weighed out into a tube of about 50 cc. capacity, and 25 cc. of decinormal iodine solution added, and the tube sealed off. In the case of benzene, the tube was sealed in an atmosphere of nitrogen; the tube was then placed in a shaking apparatus in a thermostat at 25° C.

At the end of the experiment the tube was opened and about 20 cc. were rapidly decanted off from the bulk of the carbon, and filtered through a plug of glass wool; 10 cc. of this solution were transferred to stoppered bottle and titrated with standard sodium thiosulphate solution. A fresh tube was used in each experiment.

The results are expressed throughout in terms of 100 cc. of solution. m is the number of grams of carbon accurately weighed per 100 cc. of solution; $\frac{x}{m}$ the number of grams of iodine sorbed per 1 gram of carbon; $a-x$ the final concentration of the solution in grams per 100 cc. of solution.

A corresponding series of experiments were carried out with *benzene* as solvent, and the relative results were very similar to those for chloroform, except that the actual values of $\frac{x}{m}$ were lower throughout the series.

The original solutions of iodine in chloroform and benzene were extracted with water and tested with silver nitrate, and there was no precipitate; the aqueous extracts were also neutral to methyl orange. The residues in the tubes containing the carbon were also

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extracted with water, and the extracts tested as before; again there was no precipitate with silver nitrate, and the extracts were neutral to methyl orange. Hence there was no evidence of any chemical action having taken place. In all cases, except where otherwise stated, the carbon was in the form of a finely divided powder.

The previous experiments show that the activity of the charcoal depends to some extent on its treatment before use. Where the charcoal had been heated to 120° C. it was used as soon after it had attained room temperature as possible; and in the cases where it was heated to 200° C. in vacuo, it was kept in a vacuum until required. The influence of the treatment differed in the various carbons. In the case of lampblack the value of $\frac{x}{m}$ increased from 0.0192 to 0.3784 after heating to 120° C., and to 0.3921 after heating in vacuo at 200° C., whereas in the case of sugar carbon the corresponding values of $\frac{x}{m}$ were 0.3668, 0.3868, 0.3929, respectively, the solvent being chloroform in both cases.

The coconut carbon used was from the same sample as that used in a previous work for the sorption of hydrogen. The carbon from the fruit and the shell had high sorptive powers for hydrogen, and had about equal capacity for equal weights. Their capacity for the sorption of iodine is very much lower than that of the other carbons, and, further, the finely-powdered coconut carbon is much more active than the coarsely-powdered carbon. It is important to notice that the activity of the powdered carbon from the coconut shell is much greater than that obtained from the fruit.

The experiments also demonstrate that the bulk of the iodine is "sorbed" in the first few minutes, after which the concentration of the iodine in the carbon continues to increase with time.

A further series of experiments were now carried out, in which the amount of carbon used was varied from 2 grams to 8 grams per 100 cc. of solution, and the duration of the experiments ranged from 24 hours to 5 years.

The carbon used was, in all cases, heated first to about 120° C. in an air oven until constant in weight, and finally heated in vacuo at 200° C. for 2 hours, being kept in vacuo at room temperature until required.

The constants β and $\frac{1}{p}$ are calculated from the logarithmic diagram log. $(a-x)$ log $\frac{x}{m}$ for the period 24 hours; $\frac{1}{p}$ is the slope of the line, and β is the intersection of the straightened curve with the line log. $(a-x) = 0$, that is, β is the number of grams of iodine per gram of carbon which would be in equilibrium with a solution containing 1 gram of iodine per 100 cc.

In the case of the experiments which were carried out for a period of 5 years, after 3 months the tubes were removed from the thermostat and kept at room temperature, being returned to the thermostat 3 months before they were opened.

The results are given in the following tables and shown graphically in Figs. 1—5.

Influence of (a) the amount of Carbon.
(b) Time.

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TABLE I.

Solvent Chloroform.

Time.	Lampblack as received.			Lampblack dried at 120° C.		Lampblack heated to 200° C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$ $a=1.2694$	$\frac{x}{m}$	$a-x$ $a=1.2694$	$\frac{x}{m}$	$a-x$ $a=1.2694$
5 mins.	2	0.0132	1.2430	0.3562	0.5570	0.3684	0.5326
30 „	2	0.0153	1.2388	0.3609	0.5476	0.3789	0.5116
2 hours	2	0.0171	1.2352	0.3707	0.5280	0.3862	0.4970
24 „	2	0.0192	1.2310	0.3784	0.5126	0.3921	0.4852
2 days	2	0.0218	1.2258	0.3837	0.5020	0.3981	0.4732
4 „	2	0.0241	1.2212	0.3891	0.4912	0.4042	0.4610
6 „	2	0.0268	1.2168	0.3922	0.4850	0.4048	0.4598

TABLE II.

Solvent Chloroform.

Time.	Blood Charcoal, purified and allowed to stand in a loosely stoppered bottle for 3 months.			Blood Charcoal, dried at 120° C.		Blood Charcoal, heated to 200° C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.3878	0.4936	0.4468	0.3756	0.5436	0.1820
30 „	2	0.3922	0.4848	0.4516	0.3660	0.5497	0.1698
2 hours	2	0.4006	0.4680	0.4578	0.3536	0.5568	0.1556
24 „	2	0.4064	0.4564	0.4878	0.2936	0.5597	0.1498
2 days	2	0.4118	0.4456	0.4927	0.2838	0.5646	0.1400
4 „	2	0.4173	0.4346	0.4981	0.2730	0.5669	0.1354
6 „	2	0.4227	0.4238	0.5017	0.2658	0.5682	0.1330

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TABLE III.

Solvent Chloroform.

Time.	Animal Charcoal, purified and allowed to stand in a loosely stoppered bottle for 3 months.			Animal Charcoal, dried at 120°C.		Animal Charcoal, heated to 200°C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.3254	0.6184	0.3597	0.5498	0.3698	0.5296
30 ,,	2	0.3313	0.6066	0.3645	0.5402	0.3778	0.5136
2 hours.	2	0.3412	0.5868	0.3739	0.5214	0.3852	0.4988
24 ,,	2	0.3471	0.5750	0.3802	0.5088	0.3903	0.4886
2 days.	2	0.3502	0.5688	0.3859	0.4974	0.3964	0.4764
4 ,,	2	0.3573	0.5546	0.3907	0.4878	0.4014	0.4664
6 ,,	2	0.3592	0.5508	0.3945	0.4802	0.4033	0.4626

TABLE IV

Solvent Chloroform.

Time.	Sugar Carbon, powdered, as received.			Sugar Carbon, powdered and dried at 120°C.		Sugar Carbon, powdered and heated to 200°C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.3476	0.5732	0.3658	0.5369	0.3724	0.5237
30 ,,	2	0.3520	0.5645	0.3703	0.5279	0.3802	0.5081
2 hours.	2	0.3605	0.5475	0.3798	0.5089	0.3875	0.4935
24 ,,	2	0.3668	0.5349	0.3868	0.4949	0.3929	0.4827
2 days.	2	0.3712	0.5261	0.3916	0.4853	0.3984	0.4717
4 ,,	2	0.3768	0.5149	0.3968	0.4749	0.4032	0.4621
6 ,,	2	0.3783	0.5119	0.3991	0.4703	0.4051	0.4583

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TABLE V.

Solvent Chloroform.

Time.	Coconut Charcoal from Shell, coarsely powdered* after standing two years in a loosely stoppered bottle.			Coconut Charcoal from Shell, coarsely powdered* and dried at 120° C.		Coconut Charcoal from Shell, coarsely powdered* and heated to 200° C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2 hours	2	0.0205	1.2484	0.0208	1.2480	0.0207	1.2482
24 ,,	2	0.0239	1.2418	0.0241	1.2414	0.0244	1.2408
2 days	2	0.0258	1.2380	0.0259	1.2378	0.0261	1.2374
4 ,,	2	0.0283	1.2330	0.0287	1.2322	0.0289	1.2318
6 ,,	2	0.0297	1.2302	0.0302	1.2292	0.0303	1.2290

* The average size of the particles were such as would not pass through a mesh of 2 mm. but would pass through a mesh of 4 mm.

TABLE VI.

Solvent Chloroform.

Time.	Coconut Charcoal from Shell, finely powdered, after standing for two years in a loosely stoppered bottle.			Coconut Charcoal from Shell, finely powdered, dried at 120° C.		Coconut Charcoal from Shell, finely powdered and heated at 200° C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.0539	1.1818	0.0545	1.1806	0.0544	1.1808
30 ,,	2	0.0587	1.1722	0.0595	1.1706	0.0591	1.1714
2 hours	2	0.0670	1.1556	0.0681	1.1534	0.0684	1.1528
24 ,,	2	0.1309	1.0098	0.1437	1.0022	0.1441	1.0014
2 days	2	0.1438	1.0020	0.1479	0.9938	0.1476	0.9944
4 ,,	2	0.1474	0.9948	0.1493	0.9910	0.1498	0.9900
6 ,,	2	0.1497	0.9902	0.1504	0.9888	0.1508	0.9880

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TABLE VII.

Solvent Chloroform.

Time.	Coconut Charcoal from Fruit, coarsely powdered,* after standing two years in a loosely stoppered bottle.			Coconut Charcoal from Fruit, coarsely powdered*, and dried at 120°C.		Coconut Charcoal from Fruit, coarsely powdered*, and heated at 200°C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
30 days	2	0.0041	1.2814	0.0112	1.2672	0.0142	1.2612
50 „	2	0.0080	1.2746	0.0191	1.2514	0.0223	1.2450

* The average size of the particles were such as would not pass through a mesh of 2 mm. but would pass through a mesh of 4 mm.

TABLE VIII.

Solvent Chloroform.

Time.	Coconut Charcoal from Fruit, finely powdered, after standing for 2 years in a loosely stoppered bottle.			Coconut Charcoal from Fruit, finely powdered and dried at 120°C.		Coconut Charcoal from Fruit, finely powdered and heated at 200°C. in vacuo for 2 hours.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
30 hours	2	0.0182	1.2532	0.0208	1.2480	0.0211	1.2474
30 days	2	0.0398	1.2100	0.0417	1.2062	0.0421	1.2054
50 „	2	0.0453	1.1990	0.0478	1.1950	0.0478	1.1940

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TABLE IX.

Lamp black and Chloroform.

Time, 24 hours. $\beta=0.513$ $\frac{l}{P}=0.376$			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.3921	0.4852.	0.4042	0.4610	0.4048	0.4598	0.4864	0.2966	0.5093	0.2508
4	0.2872	0.1206	0.3007	0.0666	0.3087	0.0346	0.3118	0.0222	0.3149	0.0098
6	0.1979	0.0820	0.2026	0.0538	0.2083	0.0196	0.2098	0.0106	0.2111	0.0028
8	0.1541	0.0360	0.1548	0.0310	0.1569	0.0142	0.1576	0.0086	0.1583	0.0030

TABLE X.

Blood Charcoal and Chloroform.

Time, 24 hours. $\beta=1.122$* $\frac{l}{P}=0.370$*			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.5597	0.1498	0.5669	0.1354	0.5682	0.1330	0.5701	0.1292	0.5744	0.1206
4	0.3101	0.0288	0.3131	0.0168	0.3148	0.0100	0.3159	0.0058	0.3161	0.0050
6	0.2098	0.0104	0.2102	0.0080	0.2106	0.0058	—	—	0.2108	0.0046
8	0.1573	0.0108	0.1581	0.0044	0.1580	0.0054	0.1581	0.0044	—	—

*Rejected the last measurement.

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TABLE XI.

Sugar Carbon and Chloroform.

Time, 24 hours. $\beta = 0.457$* $\frac{I}{P} = 0.213$*			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.3929	0.4827	0.4032	0.4621	0.4051	0.4583	0.4872	0.2941	0.5103	0.2479
4	0.2875	0.1185	0.3012	0.0637	0.3094	0.0319	0.3121	0.0201	0.3151	0.0081
6	0.1984	0.0781	0.2033	0.0487	0.2077	0.0223	0.2102	0.0073	0.2109	0.0031
8	0.1497	0.0709	0.1542	0.0349	0.1569	0.0133	0.1578	0.0061	0.1582	0.0029

* Rejected the last two measurements.

TABLE XII.

Animal Charcoal and Chloroform.

Time, 24 hours. $\beta = 0.467$ $\frac{I}{P} = 0.271$			Time 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.3903	0.4886	0.4014	0.4664	0.4033	0.4626	0.4898	0.2896	0.5105	0.2482
4	0.2869	0.1216	0.3003	0.0680	0.3088	0.0290	0.3109	0.0256	0.3148	0.0100
6	0.1982	0.0800	0.2026	0.0536	0.2096	0.0116	0.2103	0.0074	0.2107	0.0050
8	0.1487	0.0796	0.1531	0.0444	0.1568	0.0148	0.1579	0.0060	0.1581	0.0044

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Table XIII

Coconut Charcoal from Shell, powdered, and Chloroform.

	Time, 24 hours.		Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.1441	1.0014	0.1498	0.9000	0.1508	0.9880	0.2604	0.7484	0.3829	0.5034
4	0.1442	0.7148	0.1502	0.6888	0.1536	0.6752	0.2258	0.3660	0.2873	0.1200
6	0.1374	0.4652	0.1439	0.4262	0.1502	0.3884	0.1802	0.1880	0.1982	0.0800
8	0.1288	0.2592	0.1308	0.2432	0.1345	0.2136	0.1451	0.1084	0.1541	0.0364

Table XIV.

Coconut Charcoal from Fruit, powdered, and Chloroform.

	Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.0942	1.0808	0.2014	0.8664
4	0.0971	0.8808	0.2001	0.4688
6	0.0934	0.7088	0.1642	0.2840
8	0.0984	0.4820	0.1389	0.1580

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TABLE XV.

Lampblack and Benzene.

Time, 24 hours, $\beta=0.282$. $\frac{I}{P}=0.473$.			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.2457	0.7775	0.2544	0.7581	0.2581	0.7527	0.3594	0.5501	0.3838	0.5013
4	0.2064	0.4433	0.2141	0.4125	0.2209	0.3853	0.2235	0.3749	0.2505	0.2669
6	0.1596	0.3113	0.1638	0.2861	0.1707	0.2447	0.1734	0.2285	0.1973	0.0851
8	0.1331	0.2041	0.1375	0.1689	0.1413	0.1485	0.1439	0.1177	0.1581	0.0041

TABLE XVI.

Animal Charcoal and Benzene.

Time, 24 hours. $\beta=0.380$ $\frac{I}{P}=0.519$			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.3308	0.6073	0.3394	0.5901	0.3427	0.5835	0.4553	0.3583	0.4977	0.2735
4	0.2254	0.3673	0.2854	0.1273	0.2985	0.0749	0.3102	0.0281	0.3147	0.0101
6	0.1764	0.2105	0.1904	0.0905	0.2014	0.0605	0.2090	0.0149	0.2099	0.0095
8	0.1379	0.1657	0.1467	0.0713	0.1527	0.0473	0.1571	0.0121	0.1574	0.0097

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TABLE XVII.

Sugar, Carbon and Benzene.

Time, 24 hours. $\beta = 0.282$ $\frac{I}{P} = 0.473$			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.2496	0.7697	0.2591	0.7507	0.2608	0.7473	0.3597	0.5495	0.3842	0.5005
4	0.2065	0.4409	0.2143	0.4117	0.2215	0.3829	0.2238	0.3737	0.2507	0.2661
6	0.1595	0.3119	0.1645	0.2819	0.1710	0.2429	0.1737	0.2267	0.1974	0.0845
8	0.1332	0.2033	0.1378	0.1665	0.1415	0.1369	0.1438	0.1185	0.1524	0.0497

TABLE XVIII.

Blood Charcoal and Benzene.

Time, 24 hours. $\beta = 0.537$ $\frac{I}{P} = 0.450$			Time, 4 days.		Time, 6 days.		Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.3553	0.5886	0.3637	0.5418	0.3672	0.5348	0.4456	0.3780	0.4896	0.2900
4	0.2652	0.2084	0.2794	0.1516	0.2879	0.1186	0.2917	0.1024	0.3056	0.0468
6	0.1967	0.0890	0.1978	0.0822	0.1978	0.0822	0.2018	0.0584	0.2087	0.0170
8	0.1498	0.0708	0.1509	0.0620	0.1509	0.0620	0.1558	0.0238	0.1565	0.0172

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TABLE XIX.

Coconut Charcoal from Shell, powdered, and Benzene.

	Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.2264	0.8364	0.3451	0.5090
4	0.1893	0.5320	0.2521	0.2808
6	0.1741	0.2446	0.1867	0.1690
8	0.1378	0.1868	0.1507	0.0836

TABLE XX.

Coconut Charcoal from Fruit, powdered, and Benzene.

	Time, 6 months.		Time, 5 years.	
m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
2	0.0871	1.0950	0.1853	0.8086
4	0.0884	0.9156	0.1792	0.5524
6	0.0901	0.7286	0.1603	0.3074
8	0.0898	0.5508	0.1304	0.2266

After a period of five years, the original solutions of iodine were extracted with water and tested with silver nitrate, and there was no precipitate in either case.

The values of the constants β and $\frac{1}{p}$ obtained in the previous may be conveniently compared in the following table:

TABLE XXI.

Carbon.	Chloroform.		Benzene.	
	β	$\frac{1}{p}$	β	$\frac{1}{p}$
Lampblack	0.513	0.376	0.282	0.473
Blood Charcoal	1.122	0.370	0.537	0.450
Sugar Carbon	0.457	0.213	0.282	0.473
Animal Charcoal ..	0.467	0.271	0.380	0.519

The abnormally high value of β in the case of blood charcoal and chloroform is to be specially noted; in the case of benzene also the value of β for blood charcoal is much higher than in the other carbons.

The results obtained for coconut carbons do not admit a calculation of the constants.

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One of the most important facts indicated by the foregoing experiments is that when the concentration of the iodine in the solvent has reached a certain value, a further increase in the mass of the carbon fails to reduce the concentration *appreciably* beyond this point.

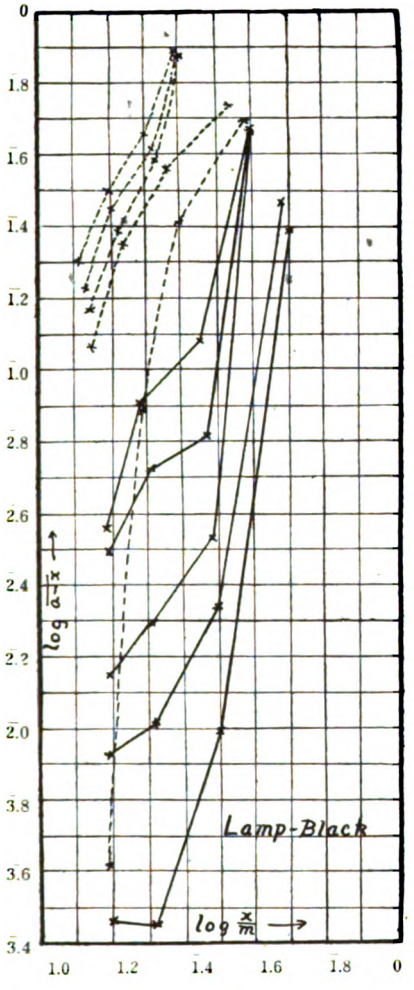

FIG. 1.

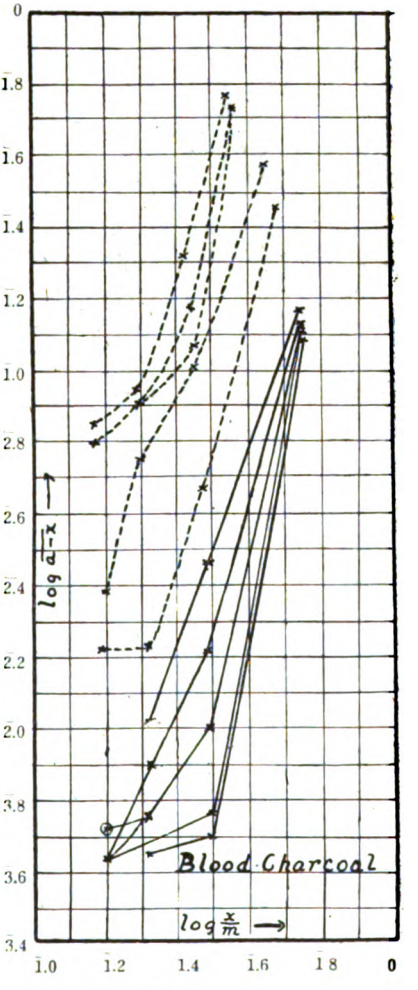

FIG. 2.

In Figs. 1—5 the continuous curves are for chloroform as solvent, and the broken curves for benzene as solvent.

The curves marked I, II, III, IV, V, are for periods 24 hours, 4 days, 6 days, 6 months, 5 years respectively.

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Influence of the Size of Carbon Particles on the Rate of Sorption.

It has already been shown that in the case of coconut carbon, from both shell and fruit, the rate of sorption of iodine is exceedingly slow when the carbon is in the form of small granules, and, further, that the rate of sorption is considerably increased when the carbon is finely powdered.

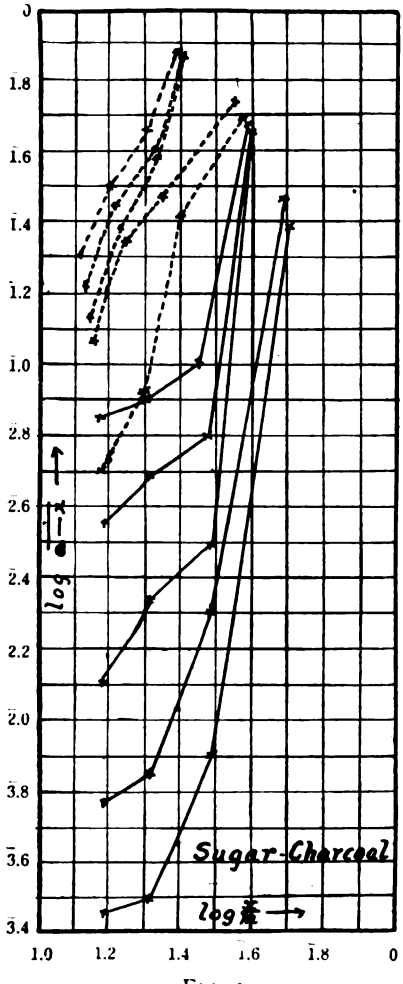

FIG. 3.

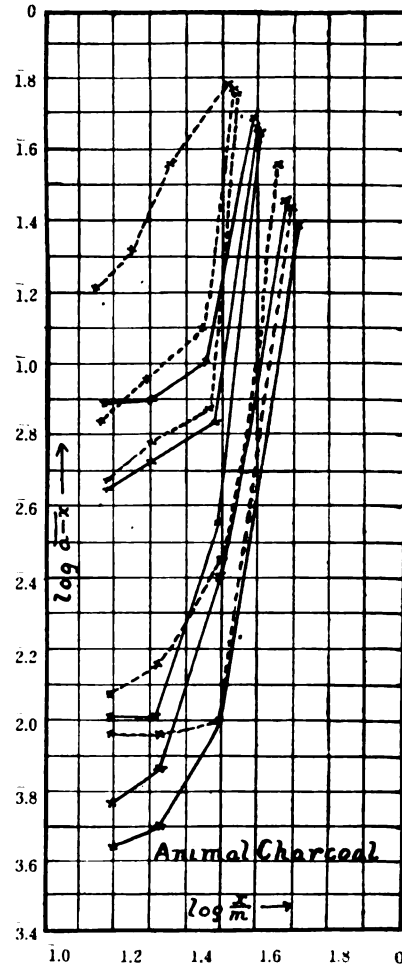

FIG. 4.

The following experiments were carried out in order to determine more fully the influence of the size of the carbon particles. The carbon chosen for this purpose was sugar carbon, and the solvent chloroform. The carbon was heated for 2 hours at 200° C. in vacuo in each case before use.

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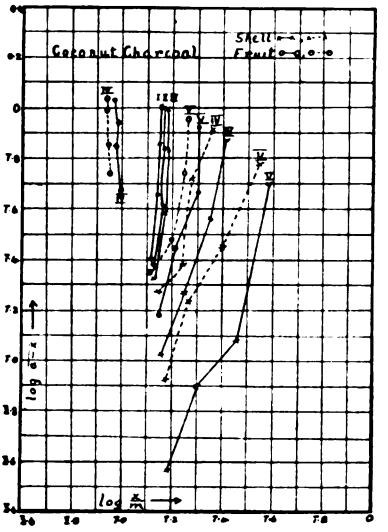

FIG. 5.

TABLE XXII.

Time.	Particles which passed through a mesh of 1.5 mm., but would not pass through a mesh of 1 mm.			Particles which passed through a mesh of 1 mm., but would not pass through a mesh of 0.5 mm.		Particles which passed through a mesh of 0.5 mm., but not through a mesh of 0.25 mm.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.3492	0.5707	0.3508	0.5675	0.3668	0.5355
30 „	2	0.3671	0.5349	0.3764	0.5163	0.3798	0.5095
2 hours	2	0.3814	0.5063	0.3842	0.5007	0.3862	0.4967
24 „	2	0.3908	0.4875	0.3918	0.4855	0.3925	0.4841

Time.	Particles which passed through a mesh of 0.25 mm., but were retained by muslin.			Particles filtered through fine muslin.		Particles filtered through fine silk.	
	m	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$	$\frac{x}{m}$	$a-x$
5 mins.	2	0.3685	0.5321	0.3733	0.5225	0.4182	0.4327
30 „	2	0.3797	0.5097	0.3818	0.5055	0.4221	0.4249
2 hours	2	0.3864	0.4963	0.3896	0.4899	0.4296	0.4099
24 „	2	0.3930	0.4831	0.3963	0.4765	0.4308	0.4075

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Sorption of Water by Carbon at Room Temperature (17° C.).

The carbon in each case was finely powdered, dried and heated to 200° C. in vacuo before use.

A weighed quantity of carbon contained in a weighing bottle was put in a desiccator, a beaker of water being also placed in the desiccator. The weight of the carbon was determined periodically. No further increase could be detected after 60 days. Then 0.5 gram of the carbon was weighed out and treated with 25 cc. of $\frac{N}{10}$ iodine solution in chloroform for 24 hours, as in previous experiments, and the value of $\frac{x}{m}$ determined.

TABLE XXIII.

Carbon.	Increase in weight per gram after exposure to water vapour for 60 days.	Value of $\frac{x}{m}$ after 24 hours uncorrected for water in carbon.	Value of $\frac{x}{m}$ corrected for water in carbon
Lampblack ...	0.35 grams.	0.1842	0.2833
Blood Charcoal ...	0.24 ,,	0.3610	0.4750
Sugar Carbon	0.14 ,,	8.2987	0.3473
Animal Charcoal...	0.18 ,,	0.2941	0.3586

Discussion of Results.

The experiments show that in the sorption of iodine by carbon a rapid condensation takes place in the first few minutes, which is followed by a much slower sorption, which continues for weeks and months, and *may* continue for several years.

True adsorption demands an almost instantaneous equilibrium; hence it would appear from the results described that the sorption of iodine by carbon involves both *adsorption* and *absorption*.

For equal weights of the carbons used the amount of iodine sorbed in 24 hours varies considerably.

In the case of blood charcoal and chloroform the sorption constitutes nearly 90 per cent. of the total iodine present, whereas in the case of powdered coconut fruit carbon it is less than 3 per cent. This wide difference cannot be explained as being due to the difference of the surface area of the two carbons, and can only be attributed to the specific action of the carbon.

Considering the influence of the solubility of the iodine in the solvent used, it will be observed that the sorption values for chloroform as solvent are higher than those for benzene. A comparison of the adsorption constant β given in Table XXI will show this more clearly.

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It has already been pointed out that there appears to be a limit to the diminution in concentration of the iodine in the liquid solvent. When this point is reached increase of mass of carbon does not produce any further *apparent* change in the concentration of the solution. Where this minimum was reached quickly, as in the case of blood charcoal, the concentration did not *appreciably* change beyond this limit after a period of five years. *The existence of these minima is probably apparent rather than real, the rate of sorption becoming exceedingly slow.*

From the figures it would appear that the ultimate curve is of a hyperbolic character. In short period experiments only the upper portion of the curve is recorded, and the results therefore give approximately a straight line. For longer periods the change in direction of the curve becomes more pronounced, finally becoming almost parallel to the horizontal axis, corresponding to an almost constant value of $a-x$ for increase of mass of carbon.

The actual value of these apparent minima will, of course, vary with the experimental conditions, being principally determined by the initial concentration of the iodine in solution, and also to a lesser extent by the duration of the experiment. The more dilute the iodine solution, the more nearly will the minimum approximate to zero.

The actual time taken to reach the minimum varies with the different carbons. In the case of blood charcoal and chloroform it appears to be reached in about six days, when the mass of the carbon is 6—8 grams per 100 cc. of solution; in other cases, where chloroform is the solvent (with the exception of coconut carbon), it is reached within five years. When benzene is the solvent, the time taken to reach the minimum is greater than in the case of chloroform.

For sugar carbon the minimum does not appear to have been attained after a period of five years, even when the mass of the carbon is 8 grams per 100 cc. The results would further indicate a higher value for the minimum in the case of benzene as solvent.

In the vicinity of the minimum the rate of sorption becomes very slow.

The evidence of minima is only shown when the mass of the carbon exceeds 4 grams per 100 cc. of solution; it is therefore reasonable to expect that the sorption would continue for a much longer period than five years in cases where the mass of carbon is about 4 grams per 100 cc. of solution. For smaller amounts of carbon the sorption may be complete before the minimum is reached.

Experiments are described which show that the size of the carbon particles influences the initial adsorption, but the carbon which had been filtered through fine silk gave a value for $\frac{x}{m}$ for 24 hours, which is still much lower than that for the same carbon after five years, hence the sorption was by no means complete.

The relative amounts of *adsorption* and *absorption* depend to some extent on the size of the particles of the carbon, but it is probable that absorption would only cease to be a factor when the carbon particles approached molecular dimensions.

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The sorption of water has been studied, and the results show that the presence of water in the carbon lowers the adsorption capacity. In the case of lampblack the effect of the presence of water is considerable. (Table XXIII).

The difference in activity of the carbons prepared from widely different sources may be due to a difference in molecular complexity of the carbon molecule. Accepting Langmuir's theory that adsorption is due to purely chemical forces, as the result of unbalanced valencies on the outer side of the solid, a difference in the orientation and complexity of the carbon molecules in the various carbons would give different values to the free valencies on the surface.

Summary.

(1) The sorption of iodine by carbon consists of a rapid surface condensation (adsorption), followed by a slow diffusion into the interior (absorption).

(2) Adsorption is nearly instantaneous, and is complete in a few hours, whereas absorption may continue for several years.

(3) The rate of sorption is dependent on the nature of the solvent and the sorbing solid.

(4) In the case of blood charcoal the adsorption is very high, whereas in the case of coconut charcoal absorption is the principal factor.

(5) The concentration of the iodine in the liquid solvent diminishes until a certain minimum is reached, after which the rate of change of concentration with increase mass of sorbing solid is so slow that the concentration appears constant.

(6) The smaller the carbon particles, the greater the initial adsorption.

(7) The presence of moisture in the carbon reduces its activity.

APPENDIX.

References.

Davis, *Trans. Chem. Soc.* (1907), *71.*
Schmidt, *Zeits. Phys. Chemie* (1910), *74;* (1911), *77.*
McBain, *Trans. Faraday Soc.* (1919), *14.*
Langmuir, *Journal Amer. Chem. Soc.* (1916), *38;* (1917), *39;* (1918), *40;* *Phys. Review* (1915), *6;* (1916), *8.*

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THE ELECTROLYSIS OF SOLUTIONS OF SODIUM NITRITE USING A COPPER ANODE.

By F. H. Jeffery, M.A.

(*A Paper read before* The Faraday Society, *June* 14, 1920, Professor Alfred W. Porter, D.Sc., F.R.S., Vice-President, *in the Chair.*)

The experiments on the electrolysis of solutions of sodium nitrite have been continued; the results obtained by using a copper anode are described in this paper.

The arrangements of the electrolysis vessel were similar to those described for use with a silver anode*; the volume of anolyte was 200 c.c., the anode area used for most experiments was 48 × 2 cms.², the temperature 15°-18°, pure sodium nitrite free from nitrate and chloride was used throughout; the reactions with solutions of concentrations 6.9 gms. $NaNO_2$ per 100 c.c. of water, 13.8 gms. $NaNO_2$ per 100 c.c. of water and 27.6 gms. $NaNO_2$ per 100 c.c. of water were examined, the formula weight of $NaNO_2$ being taken as 69.

General Description of Effects with Current of 0.16 *amp.*

Experiments were made with a current of 0.16 amp. With this current no copper was deposited on the cathode; this result was independent of the area of the anode, the smallest anode used being of area 4.7 × 2 cms.². In each case the copper went into solution, forming a dark yellow green anolyte of colour quite unlike that of cupric salts, a blue green solid was formed on the anode, and flaked off it during the progress of the electrolysis, gas was also evolved at the anode. The rapidity of formation of the solid and of evolution of gas was greater the greater the concentration of sodium nitrite in the solution used for electrolysis.

The complex copper anion produced was derived from divalent copper, sodium hydroxide gave an immediate precipitate of cupric hydroxide when added to the green anolyte, ammonium thiocyanate gave no precipitate.

With solutions of sodium nitrite of the three concentrations stated it was not found possible to isolate a sodium salt corresponding with the complex ion by evaporation in a desiccator over concentrated sulphuric acid; the effect of this was that nitric peroxide was gradually evolved, and a solid was deposited which was not crystalline, and did not contain any compound of sodium.

Trans. Farad. Soc., Vol. XV, part 3, June, 1920.

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The Potassium Lead Salt of the Complex.

A salt derived from the anolyte was isolated by the following method. After the electrolysis had continued for seven hours with constant current of 0.16 amp., the anolyte was filtered and the concentration of copper in it estimated electrolytically, the nitrite and the complex having been decomposed by heating with nitric acid. To the anolyte were added potassium nitrate and lead nitrate in the proportions given by the formula weights Cu : $_2KNO_3$: $Pb(NO_3)_2$. After twenty-four hours a crop of well-formed black crystals was obtained. These were analysed. The copper was estimated from a nitric acid solution electrolytically using Sand's electrodes, the lead was estimated as sulphate and the NO_3 groups by means of potassium permanganate after the manner described for the silver complex Na [Ag $(NO_2)_2$]. The results of these analyses for each of the three concentrations were as follow:—

Initial concent. of Na NO_3 in anolyte.	Percentage Cu in crystals.	Percentage NO_3 in crystals.	Percentage Pb in crystals
6.9 gms. per 100 cc. aq	10.16	44.10	33.12
13.8 gms. per 100 cc. aq.	10.12	44.11	33.17
27.6 gms. per 100 cc. aq.	10.15	44.18	33.11

For K_2 Pb [Cu $(NO_2)_6$] the calculated percentages are 10.17 Cu, 44.19 NO_3, 33.12 Pb.

This affords evidence that the complex copper ion is the same for each anolyte, and that it is probably Cu $(NO_2)_6$.

The Potassium Salt of the Complex.

From these black crystals the potassium salt was prepared by adding to a solution of concentration 2.5 gms. per 100 c.c. water a solution of potassium sulphate, the weight of potassium sulphate added being that necessary to precipitate the lead present in the solution. A yellow green solution was obtained. This solution was evaporated almost to dryness in an exhausted desiccator containing concentrated sulphuric acid. If the solution was kept ice-cold there was no decomposition during the concentration, but some basic material was formed on the top of the liquid if the evaporation went on at the temperature of the room. The crystals so obtained were dissolved in a small quantity of water, and the filtered solution was concentrated in the desiccator until a good crop of crystals was obtained.

These crystals were of a dark olive green colour, and very soluble in water. The percentage of copper found was 11.98 and of NO_3 was 51.86. For K_4 [Cu $(NO_2)_6$]. 2 H_2O the corresponding percentages are 11.95 and 51.89.

The Nature of These Salts.

Przibylla† obtained a salt from solutions of sodium nitrite, lead nitrate, cupric nitrate and potassium nitrate, the analysis of which shows it to be identical with the K_2 Pb [Cu $(NO_2)_6$] derived from the anolyte. He described this compound as a "triple nitrite." It seems more consistent with the results just stated to regard the compound as a salt of cupri-nitrous acid H_4 Cu $(NO_2)_6$.

†*Z. anorg. Chemie*, XV, 1897, 419.

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In terms of Werner's ideas the results may be expressed by saying that the NO_2 groups are in more intimate juxtaposition with the copper atom than the potassium and lead atoms in K_2 Pb $[Cu(NO_2)_6]$ and than the potassium atoms in K_4 $[Cu(NO_2)_6]$, the co-ordination number being six.

The Gas Evolved at the Anode.

The gas evolved at the anode was examined, the anode was shaped so that it could be placed under a test-tube filled with the anolyte, the copper wire attached to the anode being insulated with sealing wax where it came in contact with the anolyte. The gas was colourless, and was completely absorbed by ferrous sulphate solution, it reacted with pure oxygen, giving nitric peroxide. It was therefore pure nitric oxide. Its rate of evolution was slow, for a current of 0.16 amp. and an anolyte of 27.6 gms. Na NO_2 per 100 c.c. water 13-14 c.c. could be collected in an hour.

The Solid Formed at the Anode.

To obtain the solid formed at the anode it was necessary to suppress the migration of hyroxidion through the cathode pot as much as possible since this reacted with the copper complex in the anolyte and formed a layer of cupric hydroxide on the outside of the pot, the cupric hydroxide also reacted slowly with the copper complex, giving rise to an insoluble basic material, the total effect being that the concentration of copper complex in the anolyte was lowered, and the rate of formation of the anode solid decreased thereby.

To mitigate these inconveniences a form of mercury cathode was used. A flat-bottomed glass dish was placed inside the porous pot, it was of such a size that it closely fitted the pot, and its rim reached to within three millimetres below the surface of the anolyte outside the pot. The glass dish was nearly filled with mercury. A glass cylinder, open at both ends, of about half the diameter of the porous pot, was arranged so that one end dipped below the surface of the mercury, the axis of the cylinder being vertical. Inside this cylinder was water, a bundle of iron wires passed through the water into the mercury, and was connected with the lead to the negative pole of the source of current. Outside the cylinder, and bounded by the porous pot and the mercury was the catholyte of sodium nitrite. The mercury was kept in motion by a stirrer driven by a band from the anolyte stirrer.

For many subsequent experiments a simpler and in some respects more efficient device was used. A porous pot of small diameter, containing the catholyte and a platinum cathode was placed inside another porous pot of about double the diameter of the first pot, the space between the two pots was filled with an anolyte solution containing the copper complex, which had been obtained from previous electrolyses. Outside this larger pot was the anolyte to be used for making the anode solid.

The current for these experiments was 0.16 amp.

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For analysis the solid was freed from adherent anolyte by filtration, ground in a mortar with sodium nitrite solution of the same concentration as that used for the anolyte which gave rise to it, and finally washed with water to free it from sodium nitrite.

The products obtained by heating strongly were cupric oxide and nitric peroxide. The solid, therefore, appeared to be a basic cupric nitrite; the percentages of CuO and of N_2O_3 were found for solids obtained from anolytes of each of the three concentrations stated. The N_2O_3 was estimated as nitrogen, gasometrically using an Ostwald burette; about 0.5 to 0.8 gram of the solid was heated in a conical flask with 50 c.c. of water containing large excess of ammonium chloride in solution, the temperature being raised until the liquid boiled gently; this treatment completely expelled all nitrogen present as nitrite.

Specimens of the solid obtained from anolytes of each of the three concentrations gave the following results:—

Percentage of CuO ...	67.4 to 69.8
Percentage of N_2O_3 ...	32.1 to 30.0

The fact that the sum of the percentages of CuO and of N_2O_3 came to 100-0.5 was taken as a criterion that the specimen analysed was sufficiently free from adherent sodium nitrite. When the washing with water was performed rapidly, the percentages of CuO obtained were numbers close to 67.4, if the material was left in contact with water for some hours, numbers close to 69.8 were obtained.

Experiments with a Saturated Solution and Current of 0.16 *amp.*

An experiment was made with a saturated solution of sodium nitrite, the temperature being 14°, which contained 81 gms. salt per 100 gms. water. The solid obtained at the anode was of the same appearance as that from the more dilute solutions, as before the current was 0.16 amp. There was some disintegration of the anode, very finely divided copper was intermixed with the solid; this effect was probably due to the greater concentration of nitric acid at the anode.

Analysis of the solid gave the percentage of CuO 70.5, and the percentage of N_2O_3 30.4.

From this result it seems probable that the basic material is the same as that obtained from the more dilute solutions of sodium nitrite, the high percentage of CuO being due to the free copper.

With a current of 0.16 amp. no copper was deposited on the cathode.

The Nature of the Solid Formed at the Anode.

A possible interpretation of these results is that—

(i) The same basic material was formed at the anode in each case.

(ii) This material formed a solid phase in equilibrium with each of the four solutions of sodium nitrite, while the concentration of the soluble copper complex varied within wide limits.

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(iii) The material was a definite chemical individual probably identical with $Cu(NO_2)_2 CuO$, which contains 67.7 per cent. CuO and 32.3 per cent. N_2O_3.

(iv) This basic compound cannot exist in equilibrium with water, being slowly hydrolysed by it.

Experiments with a Current of 0.35 *amp.*

Experiments were made with a current of 0.35 amp., the anode area being the same as for those with 0.16 amp. The complex anion and the solid formed at the anode were the same as with a current of 0.16 amp., but with anolytes of each of the three concentrations copper was slowly deposited on the cathode. The effect of increasing the current was to increase the concentration of the NO_2 ions in the immediate neighbourhood of the anode and at the same time to increase the anode potential.

When a solution of sodium nitrite saturated at 14° was used, there was likewise a deposition of copper on the cathode for a current of 0.35 amp.

General Conclusion.

It seems probable, therefore, that the reactions at the anode can be described as follows:—

(i) The formation of the cupric anion $Cu(NO_2)_4$ from the NO_2 ions and the copper.

(ii) The decomposition of this $Cu(NO_2)_4$ by the water present giving the basic nitrite $Cu(NO_2)_2$. CuO and nitrous acid.

(iii) The slow decomposition of the undissociated portion of the nitrous acid formed giving nitric acid and nitric oxide.

(iv) Although the presence of nitric acid in contact with the copper anode must give rise to cupric ions if no current were passing, yet for the current of 0.16 amp. the concentration of such cupric ions as were formed was never sufficient for the deposition of copper on the cathode during electrolyses lasting many hours; the copper reacted with the NO_2 ions to form the complex, the anode potential remaining thereby at a low value, rather than with the NO_3 ions, which would have had the effect of raising the anode potential.

The result described in (iv) is analogous to what happened during electrolysis with a silver anode in a solution containing NO_2 and NO_3 ions.

Experiments with other metals and the same anolyte are in progress.

I am again indebted to Colonel C. T. Heycock, M.A., F.R.S., Goldsmiths' Reader in Metallurgy, for much kindness and for giving me every facility.

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THE PRESSURE VARIATION OF THE EQUILIBRIUM CONSTANT IN DILUTE SOLUTION.

By A. M. WILLIAMS, M.A., D.Sc., CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH.

(*A Paper read before* THE FARADAY SOCIETY, *June* 14, 1920, PROFESSOR ALFRED W. PORTER, D.Sc., F.R.S., VICE-PRESIDENT, *in the Chair.*)

Lewis, in his *Physical Chemistry*, Vol. II, p. 140, directs attention to the apparent difference in the expressions obtained by Planck and by Rice respectively for the variation with external pressure of the equilibrium constant of a reaction in dilute solution. The expression due to Planck is given as equation (220) of his *Thermodynamics*, and may be written

$$\frac{\delta \log K}{\delta P} = \frac{V_1 - V_2}{RT} \qquad (1)$$

where K is calculated for concentrations which are molar fractions of the total number of mols present, including the solvent and $V_1 - V_2$ denotes the volume change during the reaction. Rice (*Trans. Faraday Soc.* 12, 318) obtains a similar expression where, however, the constant refers to *volume* concentrations, whereas denoting this constant by K' we ought to have

$$\frac{\delta \log K'}{\delta P} = \frac{\delta \log K}{\delta P} - \Sigma\lambda.\beta \qquad (2)$$

where β is the compressibility of the fluid and $\Sigma\lambda$ is the change in the number of mols involved in the reaction.

Planck's proof is unimpeachable, so we must attribute the discrepancy to one of two causes:—

(i) A slip in the cycle used by Rice, or

(ii) a misinterpretation of the quantities appearing in the expression.

Mazzucchelli (*Atti. R. Accad. Lincei* 1919, 28, II, 47) assumes that the first is the cause of the divergence. Rice, in his deduction, follows the method of van't Hoff, and employs three reservoirs and an equilibrium box, all of invariable volume. His first step consists in the conversion *via* the equilibrium box of λ mols of A from the first reservoir into mols of B in the second and $\nu\mu$ mols of C in the third reservoir. The second step is compression of the system, the volumes of the reservoirs and box remaining constant. The third retransforms B and C into A, and the last step reduces the pressure to the initial value. Mazzucchelli points out that if during the changes in the external pressure we assume the volumes of the reservoirs to change with the same compressibility as the fluid, the resulting variation in the volume concentration introduces in the third step the term $\Sigma\lambda.\beta$, and thus accounts for the discrepancy. But he forgets that each reservoir is under a total hydrostatic pressure equal

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to the external pressure *plus the osmotic pressure*, and the correction thereby introduced into the second and fourth steps automatically cancels $\Sigma\lambda.\beta$. Mazzucchelli therefore fails to explain the discrepancy.

The present author finds the cause of the apparent difference to lie in a misinterpretation of the quantities appearing on the right hand side of Rice's equation. Planck discusses a one compartment system where all the components are under the same hydrostatic pressure. Thus there is no change in the volume of the solvent, which does not take part in the reaction considered, and so in this case

$$V_1 - V_2 = \Sigma\lambda v_A$$

where v_A is the molar volume (*i.e.*, the space occupied by the molecules considered apart from the solvent in which they move) of the substance A taking part in the reaction $\Sigma\lambda A = 0$.

Rice, on the other hand, considers a system of several compartments separated by semipermeable membranes, which involves a redistribution of the solvent among the compartments when a reaction takes place. If the solvent is compressible, this redistribution will involve a change in the volume of the solvent according to the hydrostatic pressures in the different compartments. This change is included in the $V_1 - V_2$ of Rice, and its value can be easily calculated as follows:—

Let us consider the total change of volume involved in the removal of λ mols of A from its reservoir, which contains a very large number l at a concentration a and an osmotic pressure p_A. It is unnecessary so far as the mere *calculation* of the volume change is concerned to conceive it as taking place by a process which is osmotically reversible. Assume the contents of the reservoir to expand under hydrostatic pressure, cut off the increment of volume, remove the λ mols of A from this, and, after further expansion, add the solvent to the main bulk. The decrement in hydrostatic pressure is the same as the decrement in osmotic pressure, namely $p_A\lambda/l$. Hence the total volume change is given by

$$\left(\frac{l}{a}.p_A.\frac{\lambda}{l}.\beta - \lambda v_A\right)\left(1 + p_A.\frac{l-\lambda}{l}.\beta\right)$$

where β is the compressibility of solvent and solution which is assumed the same, while volume is considered an additive property in dilute solution. Neglecting terms of the second order, this becomes

$$\lambda\left(\frac{p_A}{a}.\beta - v_A\right) \quad \text{or} \quad \lambda(RT.\beta - v_A)$$

Hence we see that in the $V_1 - V_2$ of Rice's equation we have the extra terms $RT\beta\Sigma\lambda$ and we write

$$\frac{\delta \log K'}{\delta P} = \frac{\Sigma\lambda v_A}{RT} - \beta.\Sigma\lambda$$

$$= \frac{\delta \log K}{\delta P} - \beta\Sigma\lambda$$

which is identical with (2).

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The value of log K' (or log K) and its variation with pressure may also be deduced from first principles as follows:—

Consider a solvent of volume W under an external pressure P and separated by a membrane permeable to solvent alone from a solution of volume U under an external pressure p + P. Let the specific volumes of the solutes and solvent be respectively v_A, v_B, v_C, w_P, and w_{P+p}. The reversible isothermal work is evidently given by

$$\delta A = (P+p)\delta U + P\delta W$$

The right hand must be a perfect differential, as must, therefore, also be

$$\begin{aligned} & U(\delta P+\delta p) + W\delta P \\ \text{or} \quad & U\delta p + (U+W)\delta P \\ \text{Now} \quad U\delta p &= U\Sigma\delta p_A \\ &= \Sigma n_A V_A \delta p_A \\ &= \Sigma n_A . \frac{RT}{c_A} . \delta c_A \\ &= RT\Sigma n_A \delta \log c_A \end{aligned}$$

where c_A is the volume concentration of A, and n_A the number of mols of A present in U.

Hence we find to be a perfect differential the expression

$$RT\Sigma n_A \delta \log c_A + (U+W)\delta P$$

and therefore also

$$RT\Sigma \log c_A \delta n_A - (U+W)\delta P$$

If the reaction considered is $\Sigma\lambda A = 0$ we have evidently

$$\delta n_A = -\lambda\delta k, \text{ etc.}$$

where k is proportional to the stage of the reaction. Hence the perfect differential becomes

$$-RT\Sigma\lambda \log c_A . \delta k - (U+W)\delta P$$

Hence $\Sigma\lambda \log c_A$ is evidently a function of P, T only (k is a pure number), and is independent of n_A, etc. We may, therefore, put

$$\Sigma -\lambda \log c_A = \log K'$$

and from the properties of a perfect differential it follows that

$$\begin{aligned} RT \frac{\delta \log K'}{\delta P} &= -\frac{\delta (U+W)}{\delta k} \\ &= V_1 - V_2 \end{aligned}$$

where V_1 and V_2 are the total volumes of the system at the beginning and end of the complete reaction. But if N is the number of mols of solvent in U and N_0 is the total number, while β is the compressibility

$$\begin{aligned} U+W &= \Sigma n_A v_A + N w_{P+p} + (N_0 - N) w_P \\ &= \Sigma n_A v_A + N_0 w_P + N(w_{P+p} - w_P) \\ &= \Sigma n_A v_A + N_0 w_P - N w_P . p . \beta \\ &= \Sigma n_A v_A + N_0 w_P - N w_P . \frac{\Sigma n_A}{N w_{P+p} + \Sigma n_A v_A} . RT . \beta \\ &= \Sigma n_A v_A + N_0 w_P - \Sigma n_A . RT . \beta \end{aligned}$$

approximately when N is large compared with n_A, etc., *i.e.*, in dilute solution.

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$$\therefore \quad \frac{\delta(U+W)}{\delta k} = \Sigma v_A \frac{\delta n_A}{\delta k} - RT.\beta\frac{\Sigma\delta n_A}{\delta k}$$

$$= -\Sigma\lambda v_A + RT.\beta.\Sigma\lambda$$

$$\text{Hence} \quad \frac{\delta \log K'}{\delta P} = \frac{\Sigma\lambda v_A}{RT} - \beta\Sigma\lambda$$

Summary.

I. The apparent discrepancy between the values of the expression for the variation with pressure of the equilibrium constant in dilute solution as obtained by Planck and by Rice respectively is shown to rest solely upon a misinterpretation of the meaning of the symbols employed by the latter. On interpreting these correctly, the apparent discrepancy vanishes.

II. Another proof of the theorem is presented, making the usual assumption that $pV = RT$.

PROFESSOR ALFRED W. PORTER (*communicated.*)

It is a matter of some surprise to me that any doubt can exist about this question as long as the perfect gas law is assumed to hold good. As Dr. Williams says, Planck's proof is unimpeachable. The other "proofs" which have been attempted are so vague that, in one case at any rate, the author of the proof was not sure himself whether he was right or wrong. The impression left on me by this last attempt is that both Mazzucchelli and he himself are right, or at least can be made right by a proper interpretation; the only difficulty is to find out with certainty what they mean and what they claim to have proved.

To come to the practical issue, nothing is proved except for conditions under which the osmotic pressure of the dissolved bodies follows the perfect gas law. It is very doubtful whether solutions so dilute as are thereby indicated are of any importance at all in connection with the possible effect of external pressure. Such cases are derivable at once from the general isothermal equations I obtained (Trans. Farad. Soc., Vol. XV, iii, p. 75 (1920). Whatever the "gas law" may be,

$$\nu_1 u_1 dp_1 + \nu_2 u_2 dp_2 \ldots\ldots - \nu_3 u_3 dp_3 - \nu_4 u_4 dp_4$$

$$= \text{constant (independent of the pressure)}$$

where u_1, u_2, etc., are molecular volumes *in the free state* of the reactants under equilibrium pressures p_1 p_2 p_3, etc., and ν_1 ν_2 are the relative numbers of molecules defining the reaction.

If the gas laws hold, then in the case of four reactants,

$$\nu_1 \log p_1 + \nu_2 \log p_2 - \nu_3 \log p_3 - \nu_4 \log p_4$$

$$= \text{constant (independent of pressure).}$$

$$= \log K_p.$$

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Again, since $p_1 = c_1 RT$, etc., where c is concentration

$$\nu_1 \log c_1 + \nu_2 \log c_2 - \nu_3 \log c_3 - \nu_4 \log c_4 = \text{constant (independent of pressure).} = \log K_c$$

K_c is the constant which Lewis and Rice considered to be dependent upon the pressure.

If with Planck we write $p_1 = x_1 p$, $p_2 = x_2 p$, etc., where p is the total pressure

$$\nu_1 \log x_1 + \nu_2 \log x_2 - \nu_3 \log x_3 - \nu_4 \log x_4 + (\nu_1 + \nu_2 - \nu_3 - \nu_4) \log p = \text{constant (independent of } p).$$

Hence if we write this

$$\log K_x + (\nu_1 + \nu_2 - \nu_3 - \nu_4) \log p = \text{constant}$$

it is seen at once that $\log K_x$ depends upon p, its rate of variation being $-\frac{\nu_1 + \nu_2 - \nu_3 - \nu_4}{p}$

The practically interesting case is when the gas laws do not hold. In this case the values of p_1, p_2, etc., need to be very carefully defined. They do not add up to the total pressure. Reference must be made to my paper for further elucidation of this more intricate case.

It is not without interest and edification to compare this problem with that of the variation of osmotic pressure with pressure in the case of a single solute. We then have, if p is the pressure to which the solution is subjected and P is the osmotic pressure,

$$\frac{dP}{dp} = \frac{u - s}{u}$$

where u = molecular volume and s, the rate of shrinkage per gram molecular of solvent removed through a membrane. When the solution is sufficiently dilute, u and s are practically equal, and therefore P does not vary with p; but in other cases P in general increases with p.

We may expect a similar complication to enter in the case of a chemically reacting mixture when the concentrations of the solutes cease to be small.

DR. A. M. WILLIAMS (*communicated reply*).

The proof given by Mazzucchelli fails for the reason stated in the paper. He makes an unjustifiable assumption in order to make Rice's result conform in the appearance of the symbols with Planck's, whereas the symbols are interpreted wrongly both by Mazzucchelli and Rice.

The K of Planck is not the same as the K_x of Professor Porter, and in equation (220) in question Planck is dealing with solutions and not with gases, and very elegantly avoids some of the difficulties referred to by Professor Porter. For example, Planck has not assumed the gas law for solutions nor introduced osmotic pressure.

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The last expression given by Professor Porter for the variation of the osmotic with the external pressure may be deduced by the method given by the author without introducing the gas law. Consider the case where only one species of solute molecule A is present. As before we have as a perfect differential

$$U\delta(p+P) + W\delta P$$

$$\text{or} \quad (U+W)\delta(p+P) - W\delta p$$

All the terms are functions of N_a, n_a, T and P only, and so is therefore

$$U+W - W\frac{\delta p}{\delta p+P}$$

Hence differentiating with respect to N we have

$$\frac{\delta U+W}{\delta N} - \frac{\delta W}{\delta N}\frac{\delta p}{\delta p+P} = O$$

$$w_{p+P} - w_P + w_P\frac{\delta p}{\delta p+P} = O$$

$$\frac{\delta p}{\delta p+P} = \frac{w_P - w_{p+P}}{w_P}$$

which is Professor Porter's expression in the present author's notation. It may be further simplified by making obvious assumptions to the form

$$\frac{\delta p}{\delta p+P} = p\beta \quad \text{or} \quad \frac{\delta \log p}{\delta p+P} = \beta$$

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A NOTE DESCRIBING MODELS ILLUSTRATING CRYSTALLINE FORM AND SYMMETRY.

DEVISED BY MISS NINA HOSALI.

(*A Paper read before* THE FARADAY SOCIETY, *Monday, June* 14, 1920, PROFESSOR ALFRED W. PORTER, D.Sc., F.R.S., VICE-PRESIDENT *in the Chair*.)

The object of these models is:—

(1) To illustrate the forms possible to crystals.

(2) To show as clearly as possible the different kinds of symmetry possessed by these forms, and

(3) To show how the forms are referred to crystallographic axes.

The method of dividing crystals into thirty-two classes, each characterised by a unique combination of symmetry elements, has been followed in designing the models. In the set of twenty-four models here exhibited, twenty-one of the more important or more difficult classes have been selected for representation. Each of the models represents some one of these classes, and shows all the symmetry elements of the class, the crystallographic axes of the system to which the class belongs, and three or more crystal forms correctly orientated with regard to the axes, and occupying the same relative positions as they would in a natural crystal. A model consists in the first place of a glass envelope, whose shape is that of some simple crystal form, and within this envelope two or three other forms are shown by means of coloured silk threads stretched over frameworks of thin wire. By this means it is easy to make the faces of one form intersect those of another, and so it is possible to make all the forms represented in one model of approximately the same size. The different forms are distinguished from one another by the use of differently coloured threads. The axes and symmetry elements are shown as follows:—

(a) *Crystallographic axes* are shown by *black threads*.

(b) The traces of the *planes of symmetry* on the glass envelope are shown by *steel wires*.

(c) *Axes of symmetry* are shown by *white threads*. (If an axis of symmetry and a crystallographic axis are coincident, the white and black threads representing them are twisted together.) The degree of symmetry possessed by an axis is indicated by small numbers printed in black attached to the thread near its ends.

(d) When simultaneous rotation about an axis and reflection across a perpendicular plane occur to produce *alternating symmetry*, the traces of the plane on the glass envelope are shown by *red and white twisted threads*, and the axis is shown by a *white thread*, its degree of symmetry being indicated by small numbers fixed to it and printed in red.

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(e) When the symmetry elements are such that the forms are *centro-symmetrical* (*i.e.*, when the faces occur in parallel pairs), a couple of *white beads* are placed at the centre of the model.

The models are intended to simplify the study of those forms which, although similar in external shape, have different relations to the crystallographic axes. For instance, in the bipyramidal class of the tetragonal system (scheelite class) we have three different orders of tetragonal bipyramids, all of similar shape, but differing in their rotation round the vertical axis. In the model illustrating this class, the three sorts of bipyramids are shown in exactly the positions they would occupy in an actual crystal, and their relations to one another and to the axes are thus clearly brought out.

In some cases a model showing a certain set of forms when in its normal position will show different varieties or modifications of those forms when inverted or rotated in some particular way. For example, the model representing the apatite class shows, in its natural position, the right 3rd order hexagonal prism and bipyramid, but when turned upside down the corresponding left-hand forms are shown. Another model, representing the +ive tetragonal scalenohedron and −ive tetragonal bisphenoid when in its normal position, shows the other varieties of these forms, namely, the −ive tetragonal scalenohedron and +ive tetragonal bisphenoid, when rotated through 90° about the vertical axis.

In the case of models illustrating enantiomorphous classes, in which the forms occur in mirror image pairs, a representation of both the members of a pair may, of course, always be obtained by reflecting the model in a mirror. Thus, the model of the quartz class shows the right 2nd order trigonal prism, the right +ive trapezohedron, and the right ditrigonal prism; while its reflection shows the left 2nd order trigonal prism, the left +ive trapezohedron, and the left ditrigonal prism.

The set of twenty-four models show, in their natural positions, over 70 different forms; but when all the modifications produced by rotating or reflecting the models are taken account of, the number of forms shown is brought up to about 140.

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APPENDIX.

The Faraday Society and the Work of the Nitrogen Products Committee.

At the General Discussion on "Basic Slags: Their Production and Utilisation in Agriculture," held on March 23rd, 1920, the following remarks were contributed by the President (Sir Robert Hadfield, Bart, F.R.S.), in introducing Professor F. G. Donnan into the Chair:—

Professor Donnan's presence this evening enables me to refer to another matter, for the successful carrying out of which we were considerably indebted to him, namely, the work of the Nitrogen Products Committee. I should like to speak about this important matter, and in so doing will be brief, and only occupy your time for a few minutes. The history of the development shows that sometimes from quite small suggestions great things spring.

As President of the Faraday Society naturally I have very much at heart that the useful and educational work we carry out should not be forgotten; that is, the President and Council wish the members to realise the important work the society is doing, even apart from meetings.

During the war there was, as you are aware, considerable shortage of certain war supplies required in the manufacture of explosives. We all heard a good deal of what Germany was doing, and after all she had little or no more knowledge than we had on the same subject, but we had not utilised it to the best advantage. I believe it was at the instance of our able secretary, Mr. F. S. Spiers, that there was first brought before the Council early in 1916 a suggestion that a special committee should be formed to study this question of nitrogen products. As President I was approached by Dr. Harker and Professor Huntington, both of whom rendered such yeoman service in the reception of this idea. A committee was formed which sat a number of times, and finally the subject was brought before the Munitions Inventions Department. This resulted in the Ministry forming a body of experts known as the Nitrogen Products Committee, to deal with this important subject. But for the work of the Faraday Society I do not think anything of this nature would have been started.

There is therefore great credit due to those who worked out the problem. As you all know, Professor Donnan, by permission of the London University authorities, was able to place his laboratory

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at the disposal of the Munitions Inventions Department. Dr. Harker, who has taken a leading and prominent part in this research, was, in his usual and indefatigable manner, able to work at the London University, the result being most important and valuable research work of the greatest service to the nation. This is shown by the voluminous final report of the Committee published a short time ago, covering nearly 400 pages.

Our work here, moreover, was of great service to the United States of America, and the value of the help we rendered has been duly recognised by that Government.

The matter being one of such vital interest to the country, and as it is important to retain this in our permanent records, I should like to read the letter of thanks I received on behalf of the Society from the Ministry of Munitions nearly four years ago, that is, on July 26th, 1916. Naturally at that particular date it was not advisable to have this mentioned publicly. The letter was as follows:—

"I am directed by the Minister to express his sense of the obligation this Ministry is under to the Faraday Society for the help it has given to the Comptroller of Munitions Inventions in the initiation of the movement which has led to the formation of what is now the Nitrogen Products Committee of the Advisory Panel.

"The Minister feels that the work that the Society has done should be recognised, and that while two of your members, Professor A. K. Huntington and Dr. J. A. Harker, who took part in the initiatory conference, are already on the Committee, neither of these represent your society officially.

"It would give the Minister pleasure if you would agree that Professor Huntington, in view of the services he has already rendered, should be considered as your representative.

"Dr. Harker, as you know, is now on the Comptroller's staff."

Also on August 21, 1916, the Ministry wrote:—

"August 21, 1916.

"I am directed by the Minister of Munitions to thank you for your letter of August 4, assuring him of your wish to assist the Ministry in every way possible, and informing him that the President and Council have agreed that Professor A. K. Huntington should represent them officially on the Nitrogen Products Committee of the Advisory Panel."

Again on July 7, 1916, the Comptroller of the Munitions Inventions Department wrote:—

"7th July, 1916.

"With reference to the letter of the 5th May from your President and other members, and to the action subsequent thereon, resulting in the formation in this department of a Nitrogen Products Committee constituted to further the research you then suggested to this department, I beg to inform you that, in view of the work which has already increased to some magnitude, I welcome your offer of further assistance."

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"You have, I learn, been for some time engaged in the collation, translation, digesting, &c., of technical literature for the preparation of your final report on nitrogen compounds, and I now suggest that you should organise one or more branches of the experimental work in prospect, such as the examination of the influence of hydrochloric acid on the Haber synthesis.

"To pay for the cost of such work, I have obtained from the Treasury the grant of a sum of £250 to cover a period of not less than six months, and I shall be prepared for you to draw upon this sum from time to time. If it can be shown that the work done justifies the expenditure, I can at a later stage put forward an application for a further sum."

On March 2 this year, as President of the Faraday Society, I received the following letter from the Ministry of Munitions, signed by Sir W. Graham Greene, the Secretary:—

"March 2nd, 1920.

"I am directed by the Minister of Munitions to forward for the information of your Society a copy of the Final Report of the Nitrogen Products Committee of the Munitions Inventions Department. As you are aware, this Report was published a few weeks ago.

"As the formation of the Nitrogen Products Committee was in a very considerable measure due to the representations made by your society to the Ministry in 1916, the Minister has no doubt that the Report will prove of special interest to yourself as President, to the Council and members of the Society.

"The Minister desires me to take this opportunity of expressing his appreciation of the valuable services rendered to the Committee by Professor A. K. Huntington, who was the official representative of your Society. As chairman of the Experiments Sub-Committee he brought his wide experience to bear upon one of the most important branches of the inquiry undertaken by the Committee. Later, as a member of the General Purposes Sub-Committee, he devoted a large amount of time to the preparation of the Final Report.

"The Minister also desires to recognise the valuable work of Dr. J. A. Harker, F.R.S., another member of the Council of your Society, who, with yourself and Professor Huntington, took a prominent part in the original negotiations, and has been in general charge of the special branch dealing with the nitrogen problem.

"It is not found possible during the war to complete the factory for fixation of nitrogen, the construction of which was commenced some two years ago.

"Your Society will, however, be interested to learn that arrangements are now on the point of being concluded whereby the synthetic ammonia factory, which had been partially erected, is to be transformed into a commercial project on a very large scale. Many other fixation schemes are also under consideration throughout the Empire. Thus your society will doubtless consider that the objects it had in view in bringing the nitrogen problem before the Ministry have been in a great measure achieved."

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I should further add that out of the work of the members of the Faraday Society with regard to the nitrogen products problem have sprung the following sectional reports:—

(1) Report on Electric Power in Production of Nitrogen Compounds, by Mr. W. R. Cooper, M.A., B.Sc.

(2) Report on Industrial Application of Rare Gases, by Dr. E. Griffiths.

(3) Report on the Manufacture of Calcium Cyanamide, by Mr. F. S. Spiers, B.Sc., Secretary of the Faraday Society.

(4) Report on the Concentration of Nitric Acid, by Mr. W. R. Bousfield, K.C., F.R.S.

(5) Report on the Utilisation of Peat, by Dr. F. Mollwo Perkin.

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No. 48.

Transactions of the Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS,

Vol. XVI. Part 3. JULY, 1921. Price 17s. 6d.

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THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS.

A GENERAL DISCUSSION

HELD BY

THE FARADAY SOCIETY AND PHYSICAL SOCIETY OF LONDON.

PUBLISHED BY THE FARADAY SOCIETY
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FOUNDED 1903.

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VOL. XVI. JULY, 1921. PART 3.

ELECTRODEPOSITION AND ELECTROPLATING.

A SYMPOSIUM AND GENERAL DISCUSSION.

An Ordinary Meeting of the Faraday Society was held jointly with the Sheffield Section of the Institute of Metals on Friday, November 19th, 1920, in the Mappin Hall of the Department of Applied Science of the University of Sheffield. A series of Papers on "ELECTRODEPOSITION AND ELECTROPLATING" were presented and discussed.

Professor C. H. Desch, D.Sc., Ph.D., Dean of the Faculty of Metallurgy, **Vice-President** of the Faculty Society, presided over the afternoon session in the unavoidable absence of the President, Sir Robert Hadfield, who had been expected to take the Chair and from whom a letter was read.

PAPERS AND DISCUSSION ON GENERAL ASPECTS OF THE ELECTRODEPOSITION OF METALS.

The **Chairman** in opening the meeting stated that the afternoon session would be devoted to papers and discussion dealing with certain general aspects of the electrolytic deposition of metals and the evening session to papers dealing more especially with the local industry of silver plating.

He called upon **Mr. W. R. Barclay** to present the introductory paper on "ELECTROPLATING FOR THE PREVENTION OF CORROSION," by Dr. Leslie Aitchison.

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Mr. W. R. Barclay in reading the paper in the absence of the author said that he was reading it because to some extent he was familiar with the author's point of view, and with the view-point, really not only of Dr. Aitchison himself, but of the Air Board officials with whom he had done a considerable amount of work. The speaker was, during the greater part of the war and still was, consulting metallurgist to the Air Board and in that capacity had examined a number of specimens of work sent in which had been plated with metals purely and simply for their use as preventives of corrosion.

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ELECTRO-PLATING FOR THE PREVENTION OF CORROSION.

By Leslie Aitchison, D.Met., B.Sc., A.I.C.

In almost all the industrial applications of iron and its alloys (*i.e.* steel) it is of great importance that steps shall be taken to ensure the permanence of the metal, or in other words that efficient protection against corrosion shall be provided. Very much the same problems arise in connection with the employment of aluminium and its light alloys. The conditions connected with iron and steel are more familiar than those with aluminium and its alloys and may most profitably be discussed here. Stainless steel is not to be considered, and therefore it may be assumed at once that all iron and all steel is affected similarly.

The usual method of protecting iron and steel against corrosion is to cover its surface with a layer of some material which will perform two functions. The first function is that the layer must in itself possess permanence in a high degree, and must not suffer or undergo disintegration or decay or be destroyed by corrosive actions, and the second function is that the layer must be one which will prevent any access to the metal beneath it of the corrosive agents which are usually destructive. These two conditions really mean that the layer must itself be able to resist attack by oxygen and moisture, weak acids, and solutions of electrolytes, and it also must be non-permeable to these agents and also have no interstices which might allow of the passage inwards of these destructive agents.

The actual reagents which have been and still are employed for the purpose of protecting iron and steel may be conveniently divided into two classes, organic and inorganic. In the former class come the paints, varnishes, and enamels, and in the second come the various kinds of metallic coatings. The second class—which is the class of interest—includes metallic coatings applied in various ways. In general the important ways of applying the metal coatings may be divided into two classes: (1) those in which the metal is put on hot, *i.e.* when molten, and (2) those in which the metal is put on cold, *i.e.* from a solution. The former includes such well-known processes as dip galvanising, tinning, and metal spraying. The latter includes the processes of zinc and nickel-plating by electro-deposition.

The cold deposition of metals as a prevention of corrosion has advanced very considerably in recent years, but probably the proportion of iron and steel parts which are protected by this method is not very high, as will be readily appreciated when the magnitude of the tin plate and galvanised sheet (corrugated iron) output is realised. In general it may be assumed that the use of the plating methods is more or less confined to articles which require special conditions of coatings, or whose nature makes them such that they can only be plated effectively—*i.e.* without spoiling the base article—in the cold. The two general advantages which can be claimed for the plating processes as regards the coatings are (1) regulated weight, and (2) superior appearance. The second advantage is by no means small and would appear to account for the large use of nickel-plated steel articles

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in bicycles, motor cycles, and automobiles. The former advantage is not very apparent in general industry, but comes quite considerably into play in aircraft—of whatever type. The weight of the coating is of course proportional to its thickness, and it is found that a coating of zinc of about three-quarters of a thousandth thick will provide a very satisfactory resistance to corrosion under aircraft conditions. It is quite impossible with a coating such as is provided by hot-dip galvanising to have a covering which is anything like so thin as this. Similarly of course the plated deposit has the notable advantage of uniformity, a property which is markedly absent from the coating produced by hot dipping. It seems probable, therefore, that the metal coatings deposited in the cold have such advantages as will result in their continued use.

The general advantage of the cold coatings with respect to the base metal is the fact that the steel or iron need not be heated at all in order to effect the deposition. For such articles as tin plate or hot dip galvanised sheet, the heating is of no importance whatever, but for such parts as aircraft steels which have been put into a definite condition of heat treatment—either by cold working or by hardening and tempering—the heating for the deposition of the metal may be dangerous and may destroy the heat treatment condition completely. If, for instance, a hard rolled steel sheet was heated for galvanising it would be partially if not wholly softened. Also a nickel chromium steel sheet, hardened and tempered, might be affected in strength by such a heating, and would almost certainly be affected in its toughness, since it would be heated to a temperature at which temper brittleness could be induced.

The metals which are most generally used for the protection of iron and steel by cold plating are zinc, nickel, tin, and copper. Writing from the point of view of the user of protective coatings and not that of the producer of the coatings, the most important metals are zinc and nickel. Whatever metal is used for the protective coatings it must possess certain properties. These properties appear to be as follows:—

1. Uniformity.
2. Permanence.
3. Good appearance.
4. Freedom from porosity.
5. Freedom from pinholes.
6. Good adhesion to base metal.
7. Reasonable ductility.
8. Freedom from scaling or flaking.
9. Penetration into all parts of a complicated surface.
10. Minimum tendency to promote corrosion of the base metal if the coating is pierced.

Most of these properties will be recognised at once as belonging to the sphere of the plater rather than to anybody else, and therefore it is not proposed to refer further to them here. The two properties which are of special interest are 7 and 10. The need for ductility in a protective coating is not always recognised and in a great number of parts the ductility is never called into play. Certain forms of material require, however, to be shaped after they have been galvanised, and it is of the utmost importance that in such circumstances the ductility of the coating shall not be inferior to that of the metal below. It is frequently necessary to bend such material over a radius equal to its thickness, and the coating must be capable of doing the same bend—that is when on the base metal,

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the actual severity of the bend for the coating being really very much less than that endured by the base metal because of the thinness of the former.

Condition 10 is a more peculiar one, and is less easy to define or to present quite accurately. By the ordinary laws of electro-chemistry certain metals (owing to their position in the electro-chemical scale) will, when joined in a galvanic circuit to iron, be anodic and others will be kathodic. Theoretically, those which are kathodic should cause the iron to go into solution, *i.e.* to corrode, whilst those which are anodic should tend to inhibit this action. Copper and zinc are two typical metals which can be considered. In theory copper should cause the iron to corrode, but zinc should protect it. The practical result which is obtained when, for instance, the protective coating on the iron or steel is destroyed or pierced at some point is that the iron corrodes whether copper or zinc is the covering layer, but that it corrodes more when copper is present than when it is covered with zinc. With a copper coating the attack upon the iron is very marked, but with zinc it is very much less noticeable, but it occurs all the same—apparently to approximately the same amount as it would if the zinc coating were absent. The corrosive action is not inhibited by the presence of the zinc, but on the other hand appears not to be accelerated as it is by copper.

In connection with the protection of iron and steel by metallic coatings the preparation of the surface which is to receive the coating is of some importance. Obviously the surface must be clean and free from rust or scale. The usual way of removing the objectionable materials from the surface is by pickling in an acid solution. Normally this is quite a reasonable thing to do, but under certain conditions and with various kinds of steel, the action of the pickling bath upon the steel is to make the metal very brittle and consequently to render it quite unfit for use in structures or for bending or shaping. It is generally thought that the brittleness is due to the absorption of hydrogen by the steel, but it appears from investigations now going on that the explanation of the action is not quite so simple. Practically the trouble can be overcome in a great degree by cleaning the articles electrolytically (*i.e.* by making them the anode in a galvanic cell). Preferably the articles may be sand blasted, but this is not always practical.

DISCUSSION.

The **Chairman:** I think it would be best if we discussed this paper now, since the ground is not quite covered by any of the subsequent papers.

Mr. Stainer Hutchins: In reference to the statement that the hardness of the metal is not wholly due to hydrogen, I think the problem is not so simple and I should like to know what the alternative is, if it is possible to explain it. Formerly it was supposed that the hardness or brittleness of the deposited metal was due to hydrogen, but the author explains at the end of his paper that the solution is not so simple as that. Will he explain some of the difficulties?

Mr. S. Field: This paper interests me very much, not because I am directly interested in the deposition of zinc for the prevention of corrosion but rather in the production of pure zinc. It appears to me that the present method of galvanising zinc by the hot process is open to much improvement. In the first place every student of chemistry knows the difference in the behaviour of pure and impure zinc against sulphuric acid—taken as an example of corrosive media.

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I imagine that in electroplating processes where zinc is deposited cold the zinc must be infinitely purer. By the hot process the zinc deposit frequently contains anything up to and even more than 2 per cent. of iron. The "protective" metal is one which is essentially susceptible to corrosion, and it seems to me that, without any experience of the cold process, there is the advantage that it must put on a very much purer metal. In the cold method it would be advantageous for those concerned to use in every case the purest metal for their anode, and to maintain the solutions in a high degree of purity. Pure zinc will stand up to any sulphuric acid.

I was glad to hear of the rigid tests with regard to ductility now being made. The Americans have always been very particular on that point and the brittleness of the zinc deposit is attributed to the presence of small quantities of cadmium. I have no personal experience of these galvanised deposits, but it seems to favour the suggestion that only the purest metal should be used for galvanising by the cold process.

The **Chairman**: Are there any members present who have practical experience of preparing galvanised coatings by electrodeposition? I know that in the shipyards the small parts used in shipbuilding are very commonly protected in this way.

Mr. S. Field: I should like if I may to supplement my remarks. I have for some time urged the use of purer zinc for hot galvanising in place of the ordinary impure spelter which contains anything up to 2 per cent. of impurities. Small scale experiments apparently yielded an inferior looking product. Presumably appearance counted for everything. On a larger scale, it was then admitted that pure zinc gave an improved appearance to the galvanised product but no attempt appears to have been made to ascertain if there is any improvement in the durability of the deposit. I feel that if such a problem were tackled by those in a position to do it we should get a good deal of light upon this question of the protection of iron and steel against corrosion by means of zinc.

Dr. W. H. Hatfield: It seems to me that the paper hardly lends itself to discussion; it is broad and covers much ground. I think if the author had restricted himself to some particular problems of interest to us in this locality we might have had a very much more intimate technical discussion. Speaking in the general way that one can, I may say I recently had the pleasure of going through several of the works in South Wales where the zinc galvanising process is in operation and also through some of the tin plating works, and I really think that if those gentlemen in this district who are interested in this question of non-ferrous coating would visit some of those works they would be surprised not only at the excellent technical manner in which the processes are conducted but they would be really surprised at the refined state in which the the tin is employed. I cannot remember now the weight of tin per pound of steel but it is very low and I understand that the coating is perfectly adherent.

There is one point the author of the paper might have very thoroughly dealt with and that is the surface of contact of the non-ferrous with the ferrous metal. A good deal of work is called for concerning the nature of the adherence of one metal to the other. Electroplating methods are peculiar to the old industries in this town, and I think this meeting will serve a very valuable purpose in focusing the attention of the silver and allied industries to what science can do for them. We have now in Dr. Desch one who is interested not only in iron and

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steel. It is necessary that other industries besides iron and steel should focus attention upon the scientific problems that affect their industry, and I hope this meeting will assist in that direction.

Mr. W. R. Barclay replied to the discussion as follows: With regard to Mr. Hutchins' question as to what other factors in addition to hydrogen may be held accountable for the brittleness of steel sheets when cleaned in acid pickling solutions I think I know Dr. Aitchison's mind a little in that direction but I ought to say in fairness to him that what he had in mind was to guard against committing himself to the view that hydrogen was the sole and only reason for such brittleness. There are as a matter of fact investigations going on in the direction of attempting to find a solution for the problem and he is aware of them and I think those who have studied the subject at all, that is from the empirical or practical point, feel that hydrogen is not the only factor that is accountable for this brittleness which is experienced.

Mr. Field has compared the electrolytic deposition of zinc and hot galvanising and one gathers from his remarks that he is strongly in favour of the cold electrolytic deposition of zinc. I think from a scientific point of view the advantage is unquestionable and one would like to call attention to the very admirable work done by Burgess in that direction in which he examined the merits of the processes. The work was only published in Germany but it is a most valuable work. He showed very clearly by a long series of experiments that, even when you get the same thickness of electrolytic zinc and the same thickness of galvanised zinc, the difference is very great. Indeed very much thinner coatings of electrolytic zinc will give much more efficient protection, at least against dilute sulphuric acid, than will a coating of four or five times the thickness when made by the ordinary hot galvanising process.

The **Chairman**: With reference to the last point that Mr. Barclay mentioned, there is a third method which often finds acceptance—the sheradising hot process, carried on at a very much lower temperature than the hot galvanising. You can apply a very thin layer and obtain quite efficient protection.

Dr. L. Aitchison (*communicated reply*): In reply to the point raised by Mr. Stainer Hutchins regarding the cause of the brittleness of steel or iron which has been pickled, I state in the paper that this is not due solely to hydrogen. As to elucidating this statement, it is scarcely possible to go fully into the matter, as the experimental work in connection with it is not yet complete. It appears, however, to have been proved quite definitely that the brittleness resulting from pickling is only found in metals of certain types of constitution.

An ordinary normal structure in plain carbon steel makes the metal in which it occurs almost immune from pickling brittleness. It is only under the most drastic conditions that such material becomes brittle. On the other hand, cold worked material is very susceptible to the effect of the acid, whilst hardened and tempered steel is not much less susceptible. The methods of removing the brittleness and the temperatures employed vary notably with the structure of the steel.

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SOME APPLICATIONS OF ELECTRO-DEPOSITION IN AERONAUTICAL ENGINEERING.

By W. A. Thain, A.M.I.C.E., late Capt., R.A.F.

For the purposes of this short paper the applications of electro-deposition in aeronautical engineering may be divided into three classes:—

1. Original processes involved in engine construction.
2. Processes designed to act as a protection against corrosion.
3. Salvage processes such as iron depositing.

Copper-depositing processes coming under Class I are the only ones considered in this paper, and three special cases are discussed, *viz.*:—

(*a*) Copper deposition as a protection against carburisation.
(*b*) Copper deposition as a means of improving heat conductivity.
(*c*) Copper deposition as a means of building up a definite constructional detail.

These three cases are considered below from the point of view of practical application only.

(*a*) Copper Deposition as a Protection against Carburisation.

In some aero-engine details, such as cam-shafts, valve-gear rocking levers, etc., it is necessary that certain parts shall be case-hardened, *i.e.*, the carbon content of that part is raised to about 0·9 to 1·0 per cent., so that on quenching from a suitable temperature, say 750° C., it shall give an extremely hard surface, and one offering great resistance to the external abrasive forces applied.

The conditions of the design require that the carbon content of the remaining portion of the article shall not be increased, so that in the final condition these portions shall be comparatively soft and ductile. These conditions are obtained by two methods:—

1. A sufficient machining allowance is made, so that where necessary the carburised material may be machined off.
2. The portions not to be carburised are covered with a protective coating impervious to carbon penetration.

Of the many protective methods tried in actual practice, the only one which has given satisfaction, is the method of copper depositing. In order to illustrate the efficiency of good copper depositing as a protection against carbon penetration, the specimen, a section through which is shown in Fig. 1, was prepared.

On a steel of very low carbon content the protective coat of copper was first deposited, this is the intermediate layer and is clearly shown in the figure. On this layer, iron was next deposited. The specimen was next carburised by the usual method of heating in a carburising medium at about 900° C. It will be seen that the deposited iron is practically saturated with carbon, but that no carbon has passed through the protective coating of copper.

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Another point of some interest is that the efficiency of the coating appears to be independent of the composition of the steel, within the limits of composition laid down for case-hardening steels.

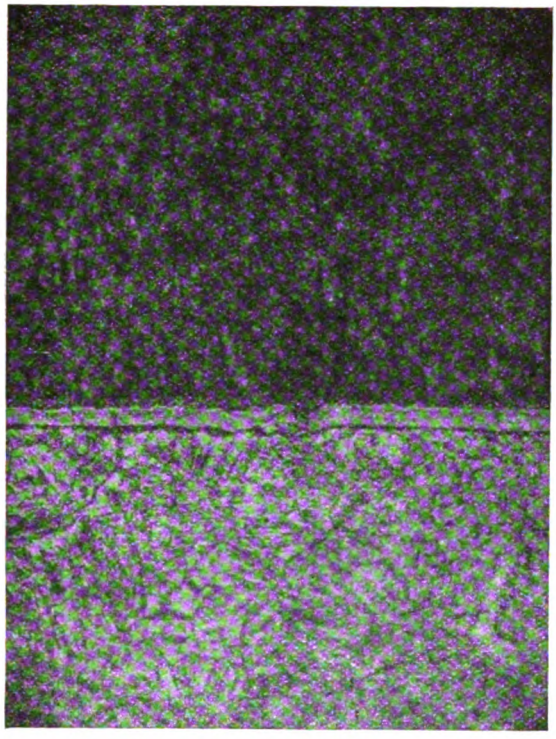

FIG. 1.—Illustrating the Efficiency of the Protective Coating of Copper.

The specification requirements as regards composition are given in the following table:—

TABLE I.

CHEMICAL COMPOSITION OF CASE HARDENING STEELS.

Specification.	S. 14.	S. 15.	S. 17.
Carbon	Not more than 0·20 per cent.	Not more than 0·15 per cent.	Not more than 0·15 per cent.
Silicon	Not more than 0·30 per cent.	Not more than 0·30 per cent.	Not more than 0·30 per cent.
Manganese . . .	Between 0·40 and 1·00 per cent.	Between 0·20 and 0·60 per cent.	Not more than 0·40 per cent.
Sulphur	Not more than 0·070 per cent.	Not more than 0·050 per cent.	Not more than 0·050 per cent.
Phosphorus . . .	Not more than 0·070 per cent.	Not more than 0·050 per cent.	Not more than 0·050 per cent.
Nickel	—	Between 2·5 and 3·5 per cent.	Between 4·5 and 6·0 per cent.
Chromium . . .	—	Not more than 0·30 per cent.	Not more than 0·30 per cent.

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It will be seen that the steels are of a fairly wide range of composition, varying from a plain carbon steel to a 6 per cent. nickel steel, although in all cases they are of low carbon content.

Fig. 2 shows the main stages of manufacture of the cam-shaft, from the original bar to the finished shaft. The parts marked A, B, C, etc., are those requiring the protective copper coating.

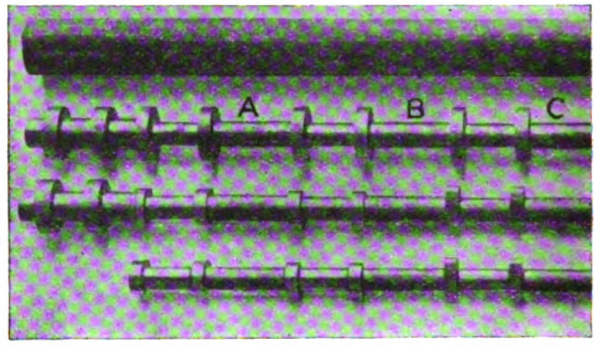

FIG. 2.

Fig. 3 shows an example of a valve rocker lever for a rotary engine on which an efficient protective coating is particularly necessary. The only portions of this lever which are carburised, are the internal surface of the bore, and the external faces of the boss. The lever rocking on a case-hardened knife-edged pin.

The top photograph on this slide shows a side view of the lever. The

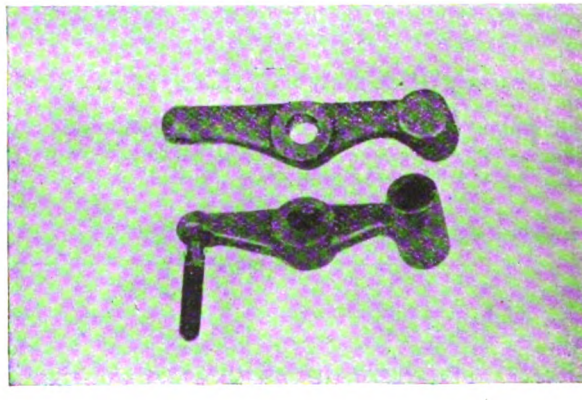

FIG. 3.

lower photograph illustrates the particular necessity for efficient protection in this example. It will be seen that the valve push rod is connected to the lever by means of a spherical-headed adjusting screw. The spherical head, working in the spherical cup at the end of the lever arm. The cup is made sufficiently deep so that connectional restraint may be obtained by riveting over the lower portion of the cup. This is clearly shown in the lower photograph. It will be evident that inefficient protection would

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mean brittle material, and would render the cup and ball method of connection impossible.

Coppering.—The methods employed for copper plating these parts have been of the usual standard types, with slight variations in detail, necessitated by the particular problem. The procedure consisting of—

1. The general cleaning operations.
2. The striking in the cyanide bath.
3. The final deposition in the copper sulphate bath.

The general principles of these processes are well known, and need not here be considered in detail. Scrupulous care, however, must be paid to the details of the processes at all stages, and in particular to cleanliness. The article to be plated must be perfectly clean both chemically and mechanically, all grease, rust, dirt, etc., must be absolutely removed. Where possible the surface of the article to be plated should be first sand-blasted with fine Calais sand, as this gives a uniform matt surface, and results in an improved adherence of the copper.

Anodes.—The anodes should be of the highest grade electrolytic copper, of say 99·7 per cent. purity, free from arsenic, antimony, and bismuth. The anode surface area should be slightly greater than the surface area of the articles to be plated (the cathode area).

In all aeronautical work a close fine-grained deposit is required and this means working with a comparatively low current density. In order to ensure uniformity of deposit, it is also necessary to arrange for the efficient circulation of the solution or for the rotation or rocking of the work to be plated.

The following is a brief outline of the process of copper plating camshafts and similar articles.

1. The shafts are carefully brushed in a caustic-soda solution of half-a-pound of caustic soda to 1 gallon of water at a temperature of not less than 80° C.
2. Brush thoroughly in cold water with pumice powder.
3. Swill in hot water and dry.
4. Cover parts not to be case-hardened with stopping-off varnish, to prevent the copper adhering. A mixture of yellow chrome and copal varnish mixed to the consistency of treacle may be used.
5. Stove at a temperature of about 180° C., till the varnish is baked hard.
6. Parts to be plated, again scoured in cold water with pumice powder to ensure that no varnish is adhering to the parts to be plated.
7. Swill in cold water.
8. Immerse in copper cyanide bath, a striking time of about three to five minutes being allowed. The parts are then copper tinted. This cyanide bath is necessary in the case of steel, as without this initial copper tinting, adherence of the copper in the copper sulphate bath cannot be obtained.

The solution may be 8 ozs. of cyanide of copper to 1 gallon of water, and should be kept at about 16° C.

A warmed and agitated bath with free cyanide is essential in order that the anodes may be kept perfectly clean.

9. Articles removed from striking bath and well swilled in cold water.
10. Place in sulphate of copper bath made up in the proportion of 34 ozs. of copper sulphate, 5 ozs. of sulphuric acid, and 1 gallon of water.

A suitable thickness of deposit for case-hardening work, is about four-thousandths of an inch.

The bath should be agitated and free acid should be present.

Both in the cyanide and sulphate baths the work is arranged between two rows of copper anodes, and the distance between the work being plated and the anodes may be from 4 to 6 inches.

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With regard to the use of a stopping-off varnish, it may be noted that the following alternative method may be adopted. The article is plated all over, and the copper deposit finally removed by means of emery from those parts of the article which have to be case-hardened. In many cases this simplifies and shortens the process, as in any case, the stopping-off varnish has to be removed before the case-hardening operation can be commenced.

Fig. 4 shows a section through a copper-deposited coating, and shows clearly the possible uniformity of deposition obtainable. The surface of the steel (the lower section of the figure) had been sand-blasted. In order to polish the section accurately it was embedded in white metal, which is shown at the top.

(*b*) Parts Plated to Improve their Heat Conductivity.

An example of the problem in which the part is plated to improve its heat conductivity may also be considered. Whether the advantages gained

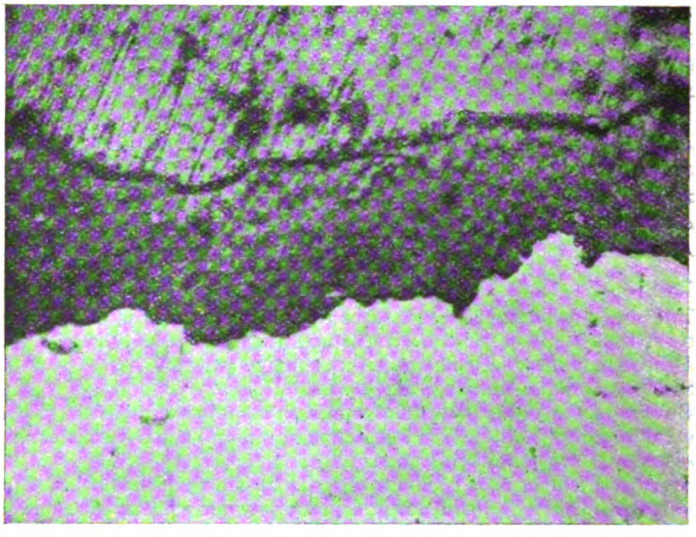

Fig. 4. (× 300.)

are sufficient to warrant the additional work and expense involved is still a debatable question and does not concern us here. The example considered is the cylinder of a radial engine. The cylinder is of the air-cooled type with the usual fins integral with the main cylinder body. The cylinder is manufactured in a plain carbon steel, and is machined from the solid The surfaces of the fins and cylinder are copper plated in order to improve the heat-conducting properties of the mass.

In this particular example the great difficulty is to obtain anything approaching uniformity of deposit on the surface of the fins.

The deposit from the heat-conducting point of view should have its maximum thickness at the root of the fin, and if anything diminish in thickness to the point.

Fig. 5 shows the actual form of the deposit at the tip of the fin, and Fig 6 shows the actual form of the deposit at the base.

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The principal causes of this inequality in the thickness of the deposit are the following :—

1. The diminution of current density owing to the opening out of the current flow lines between the fins.

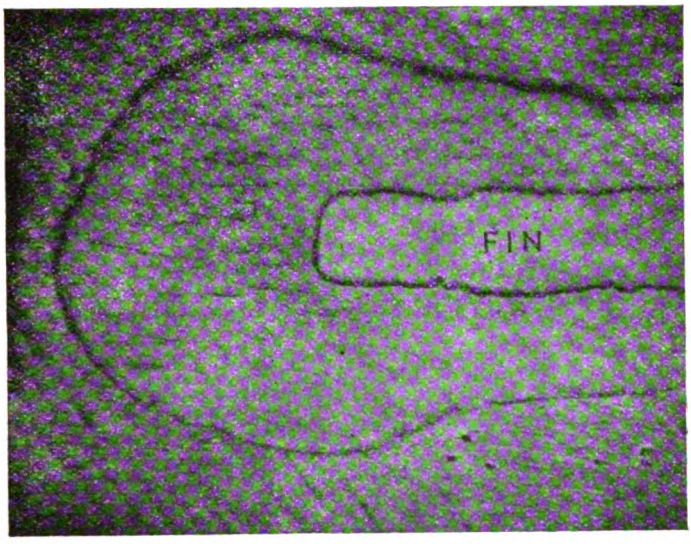

FIG. 5. (× 30.)

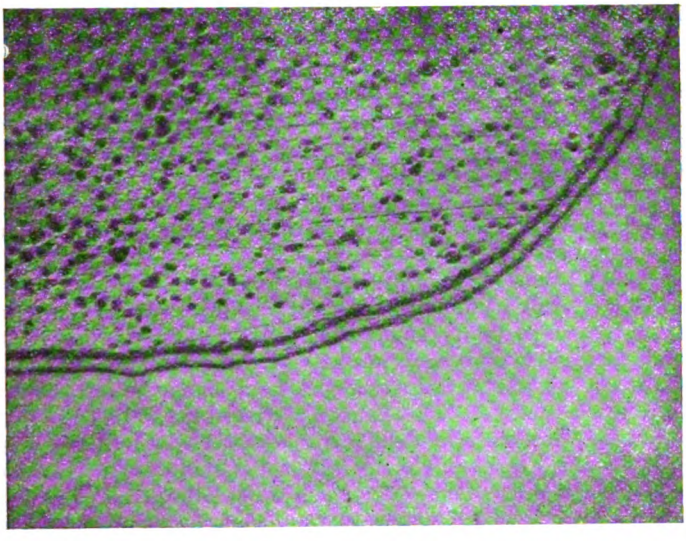

FIG. 6. (× 30.)

2. The difficulty of obtaining uniform flow of the electrolyte in the spaces between the fins.
3. Working at too high a current density.

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The trouble was to some extent alleviated by careful circulation of the electrolyte, or by rotation of the cylinder in the bath, and principally by an extension of the time of deposition, from forty to fifty hours to a period of about sixty to eighty hours, *i.e.*, by diminishing the current density.

A series of measurements on sectioned cylinders gave the following results :—

TABLE II.

Cylinder.	5th Space.		15th Space.		25th Space.	
	A. Middle of Fin.	B. Root.	A. Middle of Fin.	B. Root.	A. Middle of Fin.	B. Root.
	in.	in.	in.	in.	in.	in.
1	·0025	·0015	·0025	·002	·003	·0025
2	·004	·002	·0035	·0025	·0035	·003
3	·0035	·0025	·0032	·002	·003	·0025
4	·0035	·0025	·0035	·003	·004	·003

The above results were considered satisfactory, and batches of cylinders were passed into service if the test cylinders gave results of the above order.

Other methods of dealing with the problem will suggest themselves, and some were tried, but the results obtained are not sufficiently consistent and convincing to warrant discussion at the present stage.

(*c*).

The third case to be considered is that in which copper-depositing is used as a building-up process.

The example selected as representative of this process is the copper-deposited water jacket of the Beardmore aero-engine cylinder. The cylinder is of cast iron, and it is obvious that if the scheme of using copper-deposited water jackets can be successfully carried out, a very considerable saving in weight will result. Many hundreds of cylinders have been water jacketed by this means, and have stood the severe test of active service. The method has, therefore, been thoroughly proved and must be considered a sound practical proposition.

The general method of procedure is briefly as follows: The cast iron cylinder is first rough bored, and the skirt turned. It is then tested for strength and porosity under a water pressure of 450 lbs. per sq. in. If this test is satisfactory it is next finished, machined as far as possible, and the thread cut at the skirt to take the steel flange which secures the cylinder to the crankcase. This flange is screwed up and sweated on.

To prepare the tapered thread on the skirt and the flange, they are thoroughly cleaned, then dipped for about ten minutes in a solution of copper cyanide, a thin coating of copper being deposited. This gives a good surface for the effective adhesion of the solder when the flange is sweated on. The sweating is accomplished by heating up the cylinder and flange so as to maintain the solder in a molten condition whilst the flange is screwed hard up.

The flange is next machined up, and the casting dressed and cleaned. The cylinder is next put into a mould of cast iron, the shape of the mould

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being that of the inside of the jacket. The outlet nipple made of copper is placed in position in the mould.

A low-fusion alloy is now cast around the cylinder, the outside of this alloy corresponding to the inside of the water jacket. The low-fusion alloy used, may be either "Woods Metal," having a composition of—

Lead	25	per cent.
Bismuth	50	,,
Tin	12·5	,,
Cadmium	12·5	,,

or a special low-fusion alloy having a composition of—

Tin	33·1/3rd	per cent.
Bismuth	,,	,,
Cadmium	,,	,,

The mould is removed and the surface of the alloy dressed, finished smooth and polished, corners and sharp fillets being avoided. The surface must be free from cracks and blowholes as the copper will not deposit over such irregularities

The whole cylinder is now thoroughly scoured with pumice powder, etc., and every effort made to get it thoroughly clean, and free from grease and dirt. This is an absolutely critical operation, and the trouble and time spent on this operation is well repaid.

The inside of the cylinder is now coated with paraffin wax to protect it against attack by the acid. Plugs or stoppers are fitted to the exhaust and inlet ports, and to the bore of the cylinder, and the flanges covered with beeswax where not to be copper deposited. It is now suspended in the vat by means of brass stirrups, the suspension being such that the cylinder is free to rotate on a belt-driven vertical spindle. The spindle is revolved at about 30 r.p.m. to ensure even distribution of the deposit.

The copper anode plates are placed alongside and between each cylinder and must be of sufficient depth to extend below the lowest part of the cylinder.

The cyanide vat solution consists of—

Cyanide of Potassium	4 ozs.
Copper Sulphate	8 ozs.
Water	1 gallon.

Sulphuric acid is added according to the working of the vats. When fully covered with the cyanide deposit, the cylinder is removed, cleaned and transferred to the copper sulphate vat. The vats were of sufficient dimensions to deal with five cylinders and required an e.m.f. of 1 to 2 volts and a current of 100 amps. for five cylinders, or about 20 amps. per cylinder. Length of time in vat eighty hours for the first deposition. This gives a thickness of about 1·5 mm. and a weight of 3·5 lbs. of deposited copper.

The cylinders are removed twice a day, scrubbed, and the surface made smooth. The shape of the cylinder is such that no eddies are set up in the solution, and an easy flow of the liquid is maintained when the cylinder is revolving, otherwise unequal deposition would take place.

After the first coat the cylinder is washed and dried, and is then immersed in a bath of hot oil at 230° C. This temperature is sufficiently high to melt the "Woods Metal," which then runs out at the water inlet and outlet ports.

If the special fusible alloy is used, it can be melted out in boiling

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water, and this, of course, considerably simplifies the succeeding cleaning operations.

The bushes, nipples and studs are next screwed into place. The collars of bushes and nipples are soldered round, to fill in the sharp corners and to prepare for the second coat of copper. The inlet water connections, which are of copper and made separately, are then soldered in place.

The cylinder is now again thoroughly cleaned, and the usual precautions taken to prevent the acid attacking the steel parts, rubber tubing being placed over the studs and round the thread of the exhaust nipple.

The second coat of copper is then deposited, the time occupied being ten hours and the weight of deposited copper ½ lb. This second coating adheres firmly to the first coating, provided the conditions of cleanliness

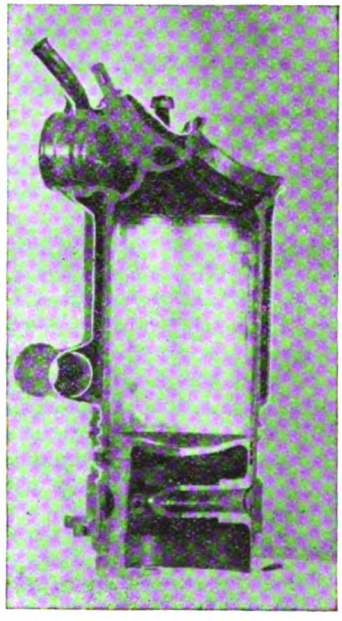

FIG. 7.

have been rigidly observed. The final thickness of the jacket wall being about 1·7 mm. The cylinder is again thoroughly cleaned and all stopping-off material removed. Machining operations are now completed and the bore finally ground.

The jacket is subjected to a water-pressure test of 25 to 30 lbs. per sq. in., and if satisfactory is passed out to service.

As will be seen from Fig. 7, corrugations are made in the sides of the jacket, and also around the sparking plug bosses in order to take up the expansion occurring under working conditions.

Fig. 7 shows a photograph of a sectioned finished cylinder and water jacket. The copper-deposited jacket is clearly shown in white in the photograph.

The above examples indicate the general lines on which the application of copper-depositing has developed in aero-engine practice.

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In conclusion I desire to express my thanks to Brig.-General R. K. Bagnall-Wild, the Director of Aeronautical Inspection, for permission to publish much of the information contained in this paper.

DISCUSSION.

Mr. D. J. Macnaughton asked what other metals besides copper were tried to prevent carbon penetration. It is generally recognised that such deposits as electrolytic iron will not be satisfactory as wearing surfaces unless they can subsequently be case-hardened, and in France where they made use of the process it appears that at some of the centres they first copper-plated and then deposited electrolytic iron on the copper. This would prevent any subsequent case-hardening, and the process was tried in some of the centres whereby electrolytic iron could be deposited direct on the steel. It would be interesting to learn what other materials were used which would prevent carbon penetration, as this would indicate any material which must be avoided as preliminary to the deposition of electrolytic iron.

The **Chairman**: I am sorry there has been no further discussion. I take it that the applications are rather too novel and we have not had direct experience of the work, but it struck me that the last application is one likely to be extended very widely because it provides a quite new method of building up elaborate parts. I should think that this is the most elaborate thing of the kind that has been done in copper deposition and it seems exceedingly interesting.

The **Chairman**: I have special pleasure in calling on Mr. Carr because he has been working in this University for a very long time. He was a practical and experienced metallurgist I suppose before most of us in this room were born and he still sets a most excellent example to the younger workers by his keenness in research. We are greatly indebted to him for always placing at our disposal his great store of experience in electrolytic deposition and kindred problems in non-ferrous metallurgy.

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THE ELECTRODEPOSITION OF COBALT.

By Byron Carr.

The following tests were carried out more than two years ago to check the results of Dr. H. T. Kalmus referred to in a paper by Mr. W. S. Burrows to the American Electro-Platers' Association.

The cobalt bath used was that numbered XIII*b* which is made up as follows :—

Five ozs. boric acid are dissolved in 5½ pints of boiling water. In this 2½ ozs. of sodium chloride are dissolved, and then 4½ lbs. of crystalline cobalt sulphate. The bath was used hot at 34° C. in these experiments, though temperatures as high as 100° F. have been recommended when working with very high current density reaching 780 amps. per. square foot with stationary electrodes, and even 1000 amps. per square foot where the solution is agitated. The electrodes on this work were stationary.

To obtain satisfactory results the cathode must be perfectly clean and smooth, all imperfections being still clearly seen after the deposition of the cobalt. The bath should be clear and excess of boric acid, if undissolved, should be filtered off. One set of experiments made with a muddy bath, possibly due to an impure sample of the cobalt salt, gave deposits which, though appearing at first sight sound and adherent, left the basis plate at once on the slightest bending. "Quicking" in a solution of mercuric cyanide was not found to be appreciably better or worse.

The deposit, which is very hard and will take on a very fine polish, is remarkably resistant to atmospheric corrosion. One polished deposit which has been lying in a chemical laboratory for over two years is still practically perfect.

It will be noted from Table I. that only the thinner deposits are adherent, and that as they thicken they begin to blister and peel off spontaneously or do so under very small bending stresses. The cobalt foil made in this way, *i.e.* by allowing a thick non-adherent deposit to peel off, may have commercial value.

This is quite in accord with the results of Dr. Kalmus, who recommends a current density of about 150 amps. per square foot, and a period of immersion of two minutes.

Some experiments were carried out to determine the influence of the composition and surface of the basis plate. The results are collected in Table II.

The deposits polish well, and though thin, have no tendency to expose the basis metal beneath. It will also be noted that in comparison, for instance, with nickel plating, these cobalt deposits are obtained very quickly indeed.

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TABLE I.

DEPOSITS IN BUFFED SURFACE OF BRASS.

No.	Current density, amps. per sq. ft.	Time, mins.	Deposit.
1	22·8	6	Fine, smooth, bright.
1*a*	22·8	16	Deposit curled off and left cathode quite clean.
2	49·2	5	Smooth, adherent deposit.
3	49·2	6	Do. do. do.
4	72	2	Do. do. do.
5	72	3	Do. do. do.
6	72	5½	Deposit peeled off cathode.
7*b*	72	5	Deposit distinctly blistered and beginning to peel off.

TABLE II.

Basis Plate.	Current density, amps. per sq ft.	Time, mins.	Deposit.
Nickel . . .	48	3½	Deposit peeled off.
Polished brass . .	48	2½	Very good adherent deposit.
Do. do. . .	81·6	2½	Polishes well. The lower C.D. gave slightly better deposit.
Brass plate coppered in alkaline copper bath	50·5	3	Good deposit.
	81·0	6	Blistered: not adherent.
Copper plate as received	110	5	Good but rough deposit.
Copper plate buffed .	71·5.	2	Very smooth deposit.

DISCUSSION.

Mr. W. R. Barclay: I am very glad to have the pleasure of opening this discussion in order first of all to pay a tribute to Mr. Carr for very valuable help at a critical time. It happened that, as Mr. Carr has said, these experiments of Dr. Kalmus and his assistants aroused a good deal of our interest, but the more valuable and perhaps the more practical result came later on. I had the responsibility at one period of the war of advising some of the Army authorities in France as to the use of electrodeposits for building up worn parts, and a very interesting discussion occurred at one stage as to whether it would be better to make permanent the plants which had already been started for the deposition of iron for such a purpose, or to adopt nickel or some alternative metal. Experiments were put in hand for nickel and then Mr. Carr's work, following that of Dr. Kalmus, suggested the possibilities of cobalt. Mr. Carr's experiments have shown that in a very considerable degree at any rate, the original results of Kalmus and his collaborators were confirmed. But I think it must be pointed out—and I think Mr. Carr will agree—that we were not satisfied at all as to the possibilities of cobalt when such a purpose was in view as the building up of worn parts to the extent of possibly from 4-thousanths of an inch to 10, 11 or even 12-thousanths. We obtained, as Mr. Carr has explained, some very good results, owing largely, if I may say so, to his extraordinary patience and manipulative skill in depositing, but I think the real difficulty with the process is the difficulty of getting these very thick deposits at high current densities to be perfectly adherent. Incidentally there is another difficulty that of course arises

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from the comparatively little knowledge we have of the metallurgy of cobalt. The trouble is to obtain anodes of a very high degree of purity, and during the last eighteen months I have had to face the thing from a purely metallurgical point of view. It was only when I had the task of producing a small quantity of rolled cobalt anodes that I realised what difficulty there was in the operation of producing rolled cobalt anodes. There again one gets a very distinct and definite lesson as to the difference between cobalt and nickel. Malleable nickel for rolling is readily produced by addition of magnesium and one would naturally conclude that cobalt could be treated similarly. An attempt to do this, however, resulted disastrously and other methods had to be sought.

Mr. S. Field: It seems to me that this subject of cobalt-plating must have a very big future on account of the wonderful properties of the deposit which are obtained and the rapidity with which work can be produced. At the Northampton Polytechnic Institute we have installed a cobalt bath in connection with the stereotyping class, and I understand that one of the large London printing houses is putting in a cobalt solution to replace nickel for facing stereos. One understands the intense hardness of the cobalt deposit and quite a few minutes immersion should suffice to give a durable deposit to stereos. I am not aware of that being done to any large extent but certainly the method is being introduced.

Mr. E. A. Smith: We are much indebted to Mr. Carr for these experiments which confirm the work of Dr. Kalmus and add valuable facts based on his long experience in the electrodeposition of metals. I should like to endorse what the last speaker has said with regard to the future. I think there is a promising future for the electrodeposition of cobalt for special purposes. The ordinary hardness of cobalt in the Brinell test is about 124 while that of nickel is only about 76·4, so that the surface of deposited cobalt should have a much greater resistance to wear than nickel. I should like to ask Mr. Carr whether he has made any attempts to determine the hardness of the cobalt deposit as compared with nickel deposits? I should also be glad to know whether he has tried to deposit cobalt on cast iron, as it is not usually easy to get a good deposit of other metals on such material. A problem connected with cast iron has recently been referred to me and it seems to me that cobalt, if it could be satisfactorily deposited on cast iron, may possibly solve this problem. I join with previous speakers in adding my thanks to Mr. Carr for his very interesting paper.

Mr. Stainer Hutchins: As there seems to be such a great difficulty in getting pure cobalt for the anode, can a satisfactory deposit be obtained with an impure anode?

Mr. Byron Carr replying to the discussion said: In regard to Mr. Smith's suggestion, I have not measured the hardness because it would be necessary to deposit the cobalt on a much stronger base metal than we have used up to the present, but I believe Dr. Kalmus does give the hardness. The hardness might be easily found when a man comes to polish the deposit; he cannot buff it like a nickel surface. I do not think there would be any difficulty in plating cast iron with cobalt. With regard to anodes, these deposits have been obtained with cast anodes which are readily obtained. They do contain some impurity, but the impurity does not amount to above 1·5 per cent. I have never attempted to determine it, but you can readily get cast anodes of cobalt, and they have given deposits which are fairly satisfactory.

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The **Chairman**: The figures given by Kalmus are only for the cast metal; he gives the Brinell hardness of cast cobalt at 124 and cast nickel as 76·4. Of course it does not follow that there would be the same difference between the electrodeposits, but I think your experiments in polishing showed a very much better hardness.

Mr. Carr: Yes, and in future I will deposit some on some stronger base and perhaps Dr. Thompson will determine its hardness.

The **Chairman**: I am sure those who look at the specimens will be struck at the beautiful character of the deposits obtained with cobalt, the very fine surface and the remarkable way in which it stands atmospheric corrosion. I was surprised to hear that it stood corrosion by fruit juice so badly; that seems a little bit unexpected; it stands quite remarkably well not only in ordinary air but in the laboratory air; I do not know the comparative acidity of gooseberry juice and the atmosphere of the Sheffield metallurgical laboratory, but these specimens have been exposed here for at least three years.

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THE COMMERCIAL ELECTROLYSIS OF ZINC SULPHATE SOLUTIONS.

By Samuel Field, A.R.C.Sc. (Lond.).

Introduction.—Some slight extension of the usual definition of electroplating is necessary to justify the inclusion of this subject in a symposium on electroplating. The problems of the deposition of compact, yet readily detachable, sheets of pure zinc from acid zinc sulphate solutions derived by the leaching of zinc ores with sulphuric acid, are of wider scope than those usually associated with the deposition of the more negative metals from either acid neutral or alkaline solutions. Partly upon the solution of these problems depends the economic success of the electrolytic extraction of zinc. This industry has, in some countries, attained considerable vogue. At Anaconda a 150 ton-a-day plant is in operation. Smaller plants are running in other parts of America while in Tasmania a plant yielding 10 tons of pure zinc per day is being extended to 100 tons per day. These are results which have been achieved only after long periods of experiment, and success or failure in one or other stage of the operation depends upon the most scientific control of mere details. One of the earliest difficulties was that of the production of sound deposits of zinc. Later troubles have, however, centred round the production of adequately pure solutions of zinc sulphate from the relatively impure materials from which it was and is sought to extract zinc. It is now proposed to illustrate some of these difficulties, more particularly in relation to the deposition processes.

Preliminary Hydro-metallurgical Processes.—Normally, sulphide ores of zinc which may be very complex by reason of admixture or combination with many other metals, notably, lead, copper, cadmium, iron, manganese, nickel, cobalt, arsenic and antimony, are after metallurgical concentration, calcined with a view to the elimination of the bulk of the sulphur as sulphur dioxide, and the conversion of the remainder to zinc sulphate in predetermined amount. The essential zinc compounds—*viz.* zinc oxide and sulphate are extracted from the calcine by leaching with acid zinc sulphate liquors outflowing from the electrolytic cells. These liquors may have an approximate composition of 2 to 3 per cent. zinc and 10·5 to 12 per cent. sulphuric acid. A judicious mixture of acid liquor and calcine economically reduces the acidity to ·1 per cent. after which complete neutralisation is effected by the addition of whiting or available zinc hydrate or carbonate. Passing over the purely chemical problems associated with this operation, a neutral solution of zinc sulphate, containing small but appreciable quantities of many metallic impurities is obtained. The solution contains practically 10 per cent. of zinc. The data given in this paper serves to emphasise the importance attaching to the processes of purifying this zinc liquor to a degree at which it becomes almost impossible to detect, by the most searching analytical tests, some of the more

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deleterious of these impurities. So pronounced are their evil effects in the subsequent electro-deposition, that it has been claimed that the zinc deposition cell is much more sensitive than chemical tests ordinarily applied. With this statement, however, we find it impossible to agree. Taking nickel as one of the common impurities in these liquors—and a highly detrimental one too—we are persuaded that the dimethyl-glyoxime test will discover one part of nickel in twenty million parts of liquor, while the maximum nickel ordinarily allowable in the liquors for electrolysis would be 1 to 2 parts per million, while having regard to commercial economy, recently devised methods of purification bring down the nickel content to one part in five million of liquor. Subsequent to adequate purification the liquors are acidified (to impart conductance) with a proportion of the

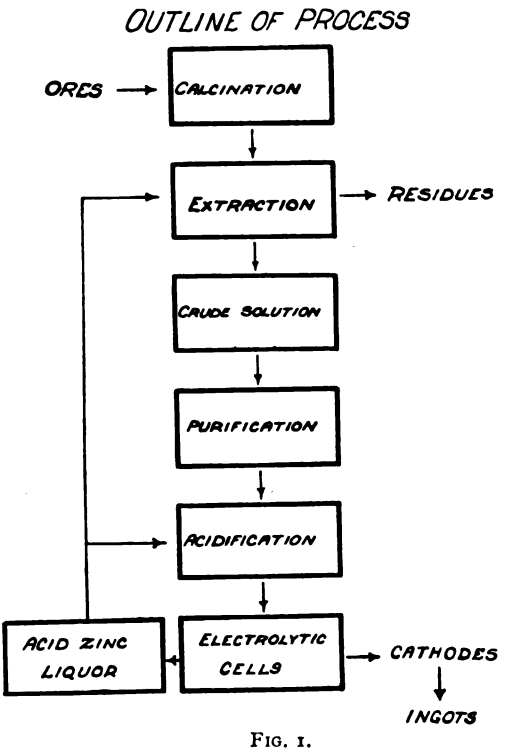

FIG. 1.

outflowing cell liquor to give a composition of 7 to 8 per cent. of zinc and 4·5 to 3 per cent. of acid. This liquor flows through suitable cascades of electrolytic cells provided with chemical lead anodes and aluminium cathodes. Steps are taken to prevent the deposition of the zinc on the edges of the cathodes so that when deposits of 24 to 48 hours run are obtained they are readily removed from, and without injury to, the cathodes. These detached deposits are then run down to ingots which, when due care has been exercised in all stages of the process, will assay 99·95 per cent. of zinc with not more than ·02 per cent. cadmium, ·02 per cent. lead, and ·01 per cent. of copper and iron together. The simple scheme of these operations is indicated in Fig. 1 which will be readily followed.

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Normally a daily output of 100 tons of zinc cathodes involves stripping about 8000 cathodes yielding 16,000 plates of zinc each weighing about 15 lb. and ·07 in. thick. The total cathode area exposed to the current amounts to 150,000 sq. ft. The plant of the Metals Extraction Corporation at Llansamlet upon which it was our privilege to carry out many tests which are here referred to, had a capacity of 1½ tons of metal per day and involved a daily stripping of 220 cathodes yielding 440 sheets each weighing 7·5 lb. and approximately $\frac{1}{16}$ in. thick.

Conditions Influencing Economic Deposition.—In this connection it must be borne in mind that success in any attempt to establish an electrolytic zinc industry in this country will be largely determined by the greatest economy in comparatively costly electrical energy—the comparison being made with the cheap hydro-electric power available in other countries. The conditions influencing energy consumption are therefore of paramount importance. At the same time economy of electrical power will have to be set against the cost of producing and handling the volumes of zinc liquors in which such economic energy consumption is to be realised, and also the capital outlay on the hydro- and electro-metallurgical plant required in these operations. Economy will therefore be determinable only when all the local conditions of cost of current and plant are known. We propose, however, to touch upon only a few of these conditions and these mainly associated with the presence of impurities.

Energy Consumption will be controlled by the average cell P.D. and current efficiency :—

$$1 \text{ ton zinc} \equiv 840000 \text{ ampere hours (approx.).}$$

$$\therefore 1 \text{ ton zinc} \equiv \frac{840000 \times \text{P.D.}}{1000} \times \frac{100}{\text{C. Eff.}} \text{ K.W.H.}$$

$$\equiv \frac{\text{P.D.} \times 84000}{\text{C. Efficiency}} \text{ K.W.H.}$$

Minimum P.D. and maximum current efficiency tend to the greatest economy in energy consumption. Taking quite normal figures an average P.D. of 3·35 volts with a current efficiency of 90 per cent. represents 3125 K.W.H. per ton of zinc cathodes.

The importance of current efficiency will be realised also from the fact that a loss of 1 per cent. in current efficiency represents, on a 100 ton plant, a ton of zinc short per day.

Again the composition and temperature of the starting and outflowing liquors has an important bearing on energy consumption. A neutral 10 per cent. zinc solution would be impracticable on account of its high resistance, and the slight sacrifice in current efficiency which results from reducing the zinc to 8 per cent. and adding 3 per cent. of acid is much more than compensated for by the considerably lower P.D. necessitated. The composition of the outflowing liquor is of even greater importance. A very marked falling off of current efficiency is likely to occur when the zinc content is down to less than 4 per cent. Under these circumstances it might be thought desirable not to proceed with the extraction of zinc beyond this point. Another consideration however comes into play. Assume that by some sacrifice of current efficiency with increased K.W.H. consumption that the zinc content could be reduced to 2 per cent. With a neutral 10 per cent. zinc liquor delivered from the purification plant, the two cases can be compared as follows :—

Case I.—Outflowing liquor with 4 per cent. zinc, the larger part of which goes back to the leaching vats.

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Extraction of zinc = 10 − 4 = 6 per cent.

Tons purified zinc liquor per ton zinc cathodes = $\frac{100}{6}$ = 16·6 tons.

Further, a quantity of zinc equal to $\frac{4}{6}$ or 66 per cent. of the output of cathodes is returned to the leaching tanks, there to be again contaminated with impurities and cyclically requiring purification with unduly high costs both of plant and operation.

Case II.—Outflowing liquor with 2 per cent. zinc, the larger part of which goes back to the leaching vats.

Extraction of zinc = 10 − 2 = 8 per cent.

Tons purified zinc liquor per ton of zinc cathodes = $\frac{100}{8}$ = 12·5 tons,

with a quantity of zinc now only $\frac{2}{8}$ = 25 per cent. of the output of cathodes going back to the leaching vats and necessitating cyclical purification.

The two cases clearly indicate the desirability of the maximum extraction of zinc from the liquor in the cells and the attainment of just those conditions which make this high extraction economically possible.

Influence of Impurities.—The presence of impurities—in some cases even in most minute traces—exercises a most important bearing on this economy. Of the impurities of which mention has already been made, the briefest statement of behaviour in the electrolytic cells must here suffice.

Copper becomes deposited with the zinc and is found in the final ingots. In the cells, however, it sets up, with the increase of acidity and temperature, a vigorous corrosion resulting in a marked re-solution of the zinc, corresponding to a much reduced current efficiency. The presence of copper may cause the entire re-solution of comparatively thick zinc cathodes. Copper must be eliminated.

Cadmium becomes deposited with the zinc and occurs in the final ingots. Being of like electro-chemical properties with zinc, it produces no such corrosion as is occasioned with copper, but assuming that the whole of the cadmium is deposited with the zinc, and this usually occurs, and that the allowable quantity in the ingot is ·02 per cent., a simple calculation will show the permissible quantity in the liquor.

Iron is not sensibly deposited. When present in the liquors, it depreciates current efficiency by anodic oxidation to ferric and cathodic reduction to ferrous.

Manganese becomes oxidised to permanganic compounds without subsequent sensible reduction of current efficiency.

Arsenic and Antimony seriously interfere with the deposition process and an increase of antimony content from ·3 to 1 part per million of liquor is said to convert a good cell operation to one which is economically impracticable.

Nickel and Cobalt in minute quantities similarly exert disastrous results in the electrolytic operation. Curiously, they behave in totally diverse manners. Each of these metals has occasioned considerable trouble in electrolytic zinc processes, the dangerous traces of the metals not being readily removed except by special purification processes. Their insidious effects are, moreover, cumulative—as the metals are not deposited in the zinc—unless special methods are employed to effect their removal in the cycle of operations. Their effects are so marked and so different that they might well provide means of identification for the small amounts concerned. The effect of nickel is observed in deep sharply cut and clean holes in the zinc deposit. That of cobalt is a general pinhole corrosion

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yielding a deposit having a structure similar to a fine lace, with dark patches on the back of the deposit.

These effects taken in conjunction with kilowatt hour consumption per ton of zinc, conclusively prove that the chief problem in electrolytic zinc is that of obtaining a sufficiently pure liquor for electrolysis.

The methods of purification which have been worked out do not come up for description here, but it may suffice to say that methods—economic methods—are available for the removal of the whole of these impurities, giving the electrolytic operation immunity from complications which in some industrial attempts seemed to have proved insuperable.

Experimental Results.—Concurrently with the production of zinc on the commercially experimental unit of $1\frac{1}{2}$ tons per day, a series of laboratory tests, to investigate problems arising, was carried out. These experi-

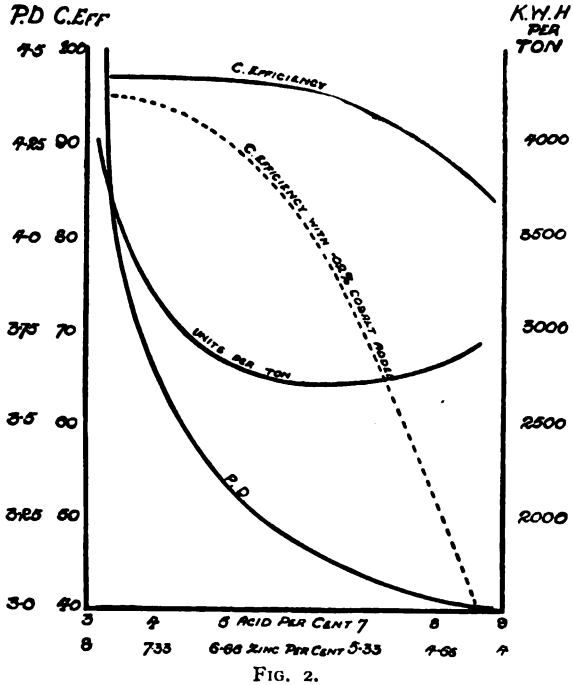

FIG. 2.

ments were effected in a series of 12 cells in cascade, reproducing approximately, though not entirely, the conditions obtaining on the larger plant. Single experiments usually extended over a period of 24 hours.

A typical series of figures obtained from a commercially pure solution are embodied in Table I. from which the curves in Fig. 2 have been plotted. The high current efficiency obtained even in a liquor containing 9 per cent. of acid is indicative of what should be obtained on a commercial plant.

A study of the K.W.H. curve indicates the possible advantage accruing from further acidification prior to electrolysis, this dilution in no way affecting the volumes of liquor in the metallurgical section of the plant. In any case the curves in Fig. 2 may be taken as typical and provide some standard for comparison.

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TABLE No. 1.

12 cells in cascade Solution pure.
Starting liquor Zinc 8·0 per cent. Acid 3·0 per cent.
Outflowing liquor ,, 4·06 per cent. ,, 8·91 per cent.
CD = 28 amperes per square foot.

Cell No.	Zinc Deposit, Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	171·7	96·8	4·63	7·83	3·26	3991
2	171·2	96·5	3·69	7·48	3·78	3195
3	171·9	96·9	3·64	7·13	4·3	3139
4	171·7	96·8	3·40	6·79	4·82	2935
5	170·7	96·3	3·24	6·44	5·34	2814
6	169·2	95·5	3·21	6·10	5·84	2810
7	168·6	95·1	3·18	5·77	6·35	2794
8	167·8	94·7	3·17	5·43	6·85	2799
9	165·1	93·1	3·13	5·10	7·34	2810
10	160·5	90·5	3·08	4·78	7·83	2845
11	152·6	87·0	3·04	4·47	8·30	2922
12	150·8	85·0	3·01	4·16	8·76	2959
Averages		93·7	3·37			3001

Table No. 2 sufficiently illustrates the trend with added impurities. In this case ·02 per cent. of cobalt is quite an unusually large amount. The very rapid falling off in current efficiency is to be noted. Little note, however, need be taken of the possibly inaccurate P.D. figure in cell No. 1.

TABLE No. 2.

Conditions same as in Table No. 1, but ·02 per cent. Cobalt added.

Cell No.	Zinc Deposit, Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	134·9	95·5	5·28	7·79	3·31	4620
2	132·8	94·0	3·4	7·38	3·93	3022
3	128·5	91·0	3·25	6·97	4·54	2985
4	127·5	90·3	3·23	6·58	5·13	2962
5	127·4	90·2	3·20	6·19	5·72	2983
6	105·0	74·4	3·20	5·83	6·26	3597
7	103·2	73·1	3·17	5·50	6·74	3603
8	94·6	67·0	3·15	5·20	7·19	3955
9	82·2	58·2	3·15	4·93	7·60	4523
10	80·1	56·7	3·13	4·68	7·98	4612
11	62·3	44·1	3·09	4·46	8·31	5855
12	59·05	41·8	3·09	4·27	8·59	6177
Averages		73·0	3·36			4074

By way of comparison the current efficiency curve from this table is inserted in Fig. 2 in a dotted line, the P.D. and K.W.H. curves being omitted.

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Coming down, however, to a more normal quantity of cobalt which may occur in commercial zinc sulphate solutions, Table No. 3 shows the results obtained with a liquor containing 10 parts of cobalt per million of liquor.

TABLE No. 3.

Effect of ·001 per cent. Cobalt.

Cell No.	Zinc Deposit, Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	175·3	96·8	3·81	7·81	3·28	3246
2	174·5	96·4	3·72	7·43	3·86	3226
3	174·2	96·2	3·51	7·05	4·43	3050
4	172·8	95·45	3·32	6·68	4·98	2908
5	172·1	95·1	3·23	6·31	5·53	2839
6	172·1	95·1	3·16	5·94	6·09	2777
7	146·6	81·0	3·08	5·59	6·61	3179
8	137·5	75·95	3·05	5·28	7·08	3357
9	126·9	70·1	3·00	4·99	7·51	3578
10	126·7	70·0	3·00	4·71	7·93	3583
11	122·4	67·7	3·00	4·44	8·34	3709
12	114·2	63·1	3·00	4·17	8·74	3975
Averages .		83·5	3·24			3285

From these figures, for which curves are not necessary, a striking observation and one which has been repeatedly made is the sudden decrease in the current efficiency figures rather than a gradual change which might be anticipated from the slowly changing conditions. This point is under close investigation. It may, however, be said that in the large scale operation the cobalt would be reduced to about one part per million of liquor.

The effect of nickel is comparable with, though perhaps worse than, that of cobalt.

TABLE No 4.

Effect of ·0005 per cent. Nickel.

Cell No.	Zinc Deposit. Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	185·2	96·96	4·25	7·82	3·27	3664
2	185	96·85	3·50	7·46	3·81	3021
3	184·7	96·7	3·46	7·10	4·35	2992
4	184·5	96·6	3·30	6·74	4·89	2856
5	184·4	96·5	3·28	6·38	5·43	2841
6	182·7	95·6	3·21	6·03	5·96	2807
7	181·4	95	3·13	5·68	6·48	2754
8	181·1	94·8	3·02	5·33	7·00	2663
9	151·2	79·2	3·01	5·01	7·49	3179
10	143·9	75·3	3·01	4·72	7·92	3342
11	140·9	73·8	3·00	4·44	8·34	3398
12	128·3	67·2	2·95	4·17	8·75	3670
Averages		88·7	3·26			3099

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Table 4 shows the effect of the addition of ·0005 per cent. (5 parts per million of liquor) of nickel. It must be pointed out that this quantity is far in excess of the amount remaining in our liquors by normal purification on the commercial scale, the methods employed reducing the nickel content to one part in five million. It must be remembered, however, that whereas in these experiments impurities were introduced singly, commercial liquors will contain traces of a number of impurities.

The beneficial effect of colloidal materials on electro-deposits is well known and Table No. 5 illustrates this in the case of the deposition of zinc from acid solutions. The solution is again that used in Table 4 with the addition of 5 parts of dried size per million of liquor.

TABLE No. 5.

Effect of addition of ·0005 per cent. Size to liquor containing ·0005 per cent. Nickel.

Cell No.	Zinc Deposit. Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	191·1	96·2	4·07	7·83	3·25	3538
2	191·6	96·4	3·66	7·49	3·76	3173
3	191·5	96·4	3·45	7·15	4·27	2991
4	191·9	96·6	3·3	6·81	4·79	2856
5	190·7	96·0	3·32	6·47	5·29	2892
6	190·6	96·0	3·26	6·13	5·81	2840
7	191·5	96·4	3·10	5·79	6·31	2688
8	189·3	95·3	3·02	5·45	6·83	2650
9	187·2	94·2	3·02	5·12	7·32	2679
10	180·9	91·04	3·00	4·80	7·80	2754
11	174·4	87·8	3·00	4·48	8·28	2859
12	171·2	86·2	2·93	4·18	8·73	2842
Averages		94	3·26			2898

The beneficial effect is marked but only of a temporary character. The maintenance of the improved results necessitates the frequent further addition of colloid. While the addition of a colloid might be made merely as a temporary expedient, it must be borne in mind that it in no way removes the cause of trouble which recurs in an aggravated form in the next cycle of operations. Indeed the only way to maintain satisfactory deposition is a high degree of purification by methods which admit of commercial application.

Conclusion.—It will be seen that a large subject has only been lightly touched upon. There is an accumulation of experience in electro-deposition for which no adequate explanation is at present forthcoming. The influence of traces of impurities (if the term is permissible) is sometimes beneficial and frequently the reverse. Without suggesting that the conditions under which zinc is electrolytically extracted are exactly comparable with those obtaining in the general processes of electro-deposition, it must be agreed that any possible light on the causes of the diseases to which deposits are susceptible may be of value in designing processes to impart immunity to such operations.

At least the lesson will be impressed that more care should be exercised over substances admitted to depositing solutions than usually obtains,

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and that no constituent should be present without a definitely known object and then in only the proportion which will yield the best result. On this score, electroplaters doubtless have a large accumulation of experience extending over many years, and a meeting of this character achieves much in offering facilities for bringing such experience to light with a view to collation, explanation, and wider application.

The author acknowledges with thanks and appreciation the painstaking assistance of Mr. W. H. Hawkes to whom he is indebted for carrying out much of the work of which that embodied in this paper is but a very small part.

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DISCUSSION.

Mr. W. R. Barclay: Mr. Field has brought forward some very interesting data. I am sorry that I have not had more time to think the question over. One thing that must be taken into consideration with regard to this and similar papers is that the problems of electrolytic refining and the problems of electroplating are essentially different and I should be rather sorry if anyone went away from this meeting with the idea that the lessons learned from electrolytic refining are necessarily to be taken as as applying to electroplating. The point of the purity of the solutions, for example, by no means relates, so far as I know, to any particular process of electroplating of metals, unless it is to a very small extent, and it is important that we should always differentiate between the two. In electrolytic refining what is required is a perfectly pure metal which has to be remelted. On the other hand for electroplating almost invariably we have to secure: first of all a perfectly adherent coating; secondly, a coating of good appearance and a coating which can, very often at any rate, be highly polished. None of these three factors has any relation to electrolytic refining.

Mr. E. A. Smith: I think we should welcome this paper because Mr. Field has touched on a branch of electrolytic deposition of metals which is sometimes neglected by those who are more directly concerned with the electroplating industry. He has dealt with a branch which has made enormous strides within recent years, possibly greater strides than in connection with the deposition of any other metal. During the last fifty years a very large number of processes have been introduced for dealing with low-grade zinc ores so that the zinc might be profitably extracted. One of the great difficulties met with in these processes was to get the zinc out in the form of metal. In most of them they only recovered the zinc in the form of oxide or in the form of a compound which was eventually converted into oxide, and it was only when the electrolytic deposition of zinc was successfully accomplished as the result of a great deal of research that it was possible to make these processes for the treatment of low-grade zinc ores a commercial success. As Mr. Field has reminded us there are large plants being erected in Tasmania and in other parts of the British Empire to deal with low-grade zinc ores, and I think that in the future the amount of zinc produced by electrolytic deposition processes will be a very formidable competitor to the present smelting processes. I have been very much interested in the paper and

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the author has pointed out some of the difficulties which have to be overcome in making the electrodeposition of metals for extraction purposes on a large scale a commercial success.

Mr. Turner: I should like to ask Mr. Field whether he can tell us why such a remarkable improvement takes place on the addition of ·0005 per cent. of size to the solution? Was it a question of increased or decreased conductivity or has Mr. Field any theory which he cares to expound?

The **Chairman:** I should like to ask one question. Within recent years there has been a considerable quantity of high-grade zinc produced in this country by electrolytic processes, but I believe it is a fact that all the firms who have been manufacturing zinc by that process have recently closed down their plant. Can Mr. Field throw any light upon this practical failure of the process within recent years? There is also a scientific point which struck me as of considerable interest; the difference in the behaviour of nickel and cobalt. From our studies of chemistry we have always been led to understand that these two metals were so closely alike as to be almost indistinguishable. But in iron and steel metallurgy one finds a very considerable difference in the behaviour of the two, and here it comes out again. It would seem that the similarity of these two closely allied metals was not so great as one has been led to expect.

Mr. Macnaughton: I would supplement that previous question by asking if the effect is so pronounced in the case of nickel as cobalt and whether the effect is permanent or whether additions have to be made from time to time?

Mr. S. Field, in reply to the discussion said: This subject is not one of electrolytic refining but of extraction. In the early days of this zinc metallurgy the problem was to get a pretty good deposit, and the next to get out the zinc in a pure form and to get it out efficiently. I am not able to offer any explanation of the wonderful effect of those colloids. Many of us are awaiting a simple yet adequate explanation of apparently very simple effects which every electroplater knows. Dr. Desch referred to the apparently wonderful difference between cobalt and nickel. I am at a total loss to account why these two seemingly similar substances should act so differently. In reply to Mr. Macnaughton, I may say that the use of colloids is permissible only as a temporary measure. What is wanted is to get out the maximum of zinc from solutions highly purified; it is not a matter of covering up impurities. With regard to Dr. Desch's question it should be remembered that no large scale on commercial plant has yet been put down in this country. Certain experiments carried out in South Wales by one of the zinc firms produced between 100 and 200 tons of the pure metal. Then the experiments closed down with a view to building upon a more convenient site and on a very much larger scale. You could not produce electrolytic zinc commercially in this country with a plant of 1½ tons a day capacity; the nearer it gets to 20 or even 100 tons a day the better the prospect will be.

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THE DEPOSITION OF GOLD-SILVER ALLOYS.

By Samuel Field, A.R.C.Sc. (Lond.).

Introduction.

The composition of electro-deposited alloys has not claimed wide attention, though such deposition has long been established practice. In two previous papers alloys of copper and zinc and silver and copper have been dealt with. The investigation has now been carried a step further in a study of the conditions influencing the simultaneous deposition of silver and gold.

Both of these highly electronegative metals are deposited singly with ease. Further, it is a well-known fact, and one which it is now proposed to follow quantitatively, that the colour of gold deposits is considerably influenced by the presence of impurities such as silver and copper. This fact is utilised in the production of coloured deposits, a gilding solution containing 10 to 20 per cent. of its metal content of copper yielding a pleasing "red gold," while a smaller addition of silver cyanide produces the familiar "green gold". These cases provide a marked contrast with that of silver and copper, for, in a previous paper,[1] it has been shown that considerable difficulty is experienced in the simultaneous deposition of these metals, and analytical methods of separation are even possible. With gold, however, copper and silver are readily precipitated electrolytically from the cyanide solution, and from this it would appear that gold occupies an intermediate position being positive to silver and negative to copper.

In spite of the use of these coloured deposits for so long no attempt seems to have been made to ascertain by systematic experiment the influence of conditions upon the composition of the resulting alloy. This we have essayed to do, supplementing the results of laboratory experiments by the analysis of a series of deposits obtained on prepared electrodes under commercial conditions in a London workshop.

The P.D.'s of the three metals in cyanide solution are given by Christie[2] as follows:—

	N. KCN.	$\frac{N}{10}$ KCN.	$\frac{N}{100}$ KCN.	$\frac{N}{1000}$ KCN.
Copper	·81	·62	·37	·16
Gold	·37	·23	·09	– ·38
Silver	·33	·15	– ·05	– ·36

If then copper and silver present difficulties in simultaneous deposition, and this has been previously confirmed, so also it might be anticipated that

[1] *Trans. Faraday Society*, vol. vi., p. 1.
[2] *Amer. Inst. Mining Eng.*, Sept., 1899.

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difficulty should be experienced in the deposition of alloys of copper and gold. This matter is reserved for treatment in a further paper.

Method.—Solutions of the double cyanides being invariably used in the deposition of silver and gold, these have been exclusively examined. Preliminary experiments were made with the quantitative deposition of gold before dealing with the alloy solution. The results obtained show that a good cathode efficiency is only obtained with solutions much stronger than those ordinarily employed in the gilding process, and for the greater part of the work a solution containing 19·7 grams. of gold per litre [= 2·9 ozs. troy per gallon] was used. The cathode efficiency was obtained by reference to the copper deposited in a coulomb meter in series and the following figures show the order of the efficiencies obtained, being preceded by the equivalents of the metals :—

	Copper		*Silver.*	*Gold*
	from sulphate.	from cyanide.		from cyanide.
Chemical equivalent . . .	31·8	63·6	108	197
or as	1	2	3·396	6·195
Grams per ampere-hour . . .	1·182	2·364	4·024	7·35

TABLE I.

(Current Efficiencies in Warm Moving Gilding Solution Using Platinum Anode.)

Experiment.	Current (amperes).	Copper from Coulomb Meter.	Gold.	
			Deposit.	Cathode Efficiency.
1	·25	·1436	·0522	5·88
2	·50	·1432	·0692	7·80
3	·60	·1856	·4493	39·0
4	·75	·1478	·4858	53·2
5	·75	·1424	·5232	59·3
6	·75	·1524	·6608	70·0

It was thus early learned that good efficiencies are best obtainable with moderately high current densities, and a number of other important points soon came to light. Thus with low current densities very little deposition occurs even in relatively strong solutions. Further the deposit of gold is susceptible to solution in the cyanide liquid causing a depreciation in the efficiency. Still further, some difficulty was encountered in selecting a cathode material which would be most suitable for the subsequent deposition of the alloys. Ultimately for the reasons given later, assay lead foil was selected.

The quantitative deposition of silver offers no difficulty given fairly strong solutions of the metal. Thus, using a semi-normal solution of the double cyanide (approximately 8 ozs. metal per gallon) the following results were obtained :—

Experiment.	1	2	3
Cathode efficiency . . .	97·8	96·5	98·8
Anode ,, . . .	117	93·6	95·8

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Some loss, however, was persistently recorded in subsequently cupelling the deposits made on lead cathodes. Such differences were:—

Weight of Silver Deposit.	Weight of Silver after Cupellation.	Loss.	Percentage Loss.
·3660	·3617	·0043	1·17
·5725	·5678	·0047	·82
·5408	·5336	·0072	1·33

These losses, however, include a small loss by corrosion of the lead cathodes, but in view of the method subsequently adopted in the determination of gold would be negligible.

Similar, though much smaller, errors for gold were observed as follows:—

Weight of Gold Deposit.	Weight after Cupellation.	Loss.	Percentage Loss.
1·3022	1·3010	·0012	·09
·6544	·6506	·0038	·58
·4865	·4848	·0017	·35

but as these figures also include whatever corrosion of the lead cathode had occurred they were disregarded.

Deposition of Gold-Silver Alloys.

(1) *The solution* first used in this work was obtained by mixing calculated volumes of decinormal gold and seminormal silver double cyanide solutions, each containing a minimum of free cyanide. The mixed solution contained gold and silver in the proportion of 2 : 1, 21·6 grams of the mixed metals per litre [= 3·18 ozs. troy per gallon].

It should be noted that green gold solutions vary very widely in their composition, one ordinary recipe being:—

Gold 1 dwt.		2·74 grams.
Silver ½ ,,	corresponding	·46 ,,
Potassium cyanide 1 oz.	to	50 ,,
Water 1 pint		1 litre.

The generally low metal-content is noticeable.

(2) *Choice of a Cathode.*—The subsequent analysis of the deposit influences this choice. Deposits readily attacked by a single acid are conveniently made on platinum gauze. The use of platinum, however, is precluded in this case. In view of a simple method of analysis of deposits by cupellation, assay lead offered great advantages. Chemical cleaning and drying prior to weighing did not prove satisfactory, the deposits invariably stripping owing to the difficulty of preventing oxidation during drying. Coppered lead, and silvered lead cathodes were tried, but proved impracticable owing to excessive corrosion in the cyanide liquid, while plain lead was almost unaffected. Cathodes were therefore prepared by carefully scraping off the surface of the sheet, in preference to chemical cleaning and scouring with pumice. Adherent deposits were thus obtained though on drying, a decided increase in temperature was likely to effect separation of lead and deposit owing to the considerably differing coefficients

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of superficial expansion, *viz.* : gold, ·0000294; silver, ·0000382; lead, ·0000572; or, as 1 : 1·3 : 2. Flaking away of the deposit from the lead in the early stage of heating during cupellation, was avoided by wrapping the dried and weighed deposit in more lead foil previous to rolling up for cupellation. The separation of lead and deposit could in some cases be distinctly discerned as a cracking noise. The corrosion of lead in the cyanide solution amounted in several trial experiments to only decimal parts (·5 or ·6) of a milligram, and this was, in view of deposits of a metal with so high an equivalent as that of either silver or gold, regarded as negligible. Silvered lead cathodes, previously referred to, seemed to offer considerable advantages: (1) In the greater adherence of the deposit, and (2) in that sufficient silver could thus be used to produce a parting mixture with the subsequent deposited alloy after cupellation. Excessive corrosion, however, amounting to 2 to 3 centigrams on the small cathodes in use, militated against their use.

(3) *Choice of Anode.*—The use of gold and silver anodes is in this case impossible owing to (*a*) their more than efficient electrolytic corrosion, leading to an increase of the metal content of the solution, and (*b*) the impossibility of thus arranging for a constant ratio of gold to silver in the bath.

Platinum anodes were therefore employed, and the loss of metal from the solution was made good before a succeeding experiment by the addition of approximately computed volumes of standard gold and silver cyanide solutions. In some cases the analysis of a deposit was completed before the next experiment was arranged, and even where this was not possible, a rough idea of the silver and gold withdrawn from the solution could easily be gained and made good. Slight changes in composition in the relatively large volume of solution are negligible in single experiments, but errors are prevented from accumulating by correcting the amounts as the analytical results were obtained. Thus in a particular case noted the following figures show the approximately computed quantities added, and the correct quantities calculated from the analysis.

In successive experiments :—

Volumes of Standard Solutions (c.cs.).

	Added by Rough Computation.		Required by Calculation from Analysis.	
	Gold.	Silver.	Gold.	Silver.
	15	5	16·1	4·9
	15	7·5	14·7	6·8
	15	5	15·1	6·0
Totals	45	17·5	45·9	17·7

The solution was then corrected after the three experiments by the addition of ·9 c.c. gold solution, and ·2 c.c. silver solution to the 600 c.c. of solution in use.

Slight increase of concentration by slow evaporation at 50° C. at which some of the experiments were made was practically compensated by these additions of solutions.

(4) *Analysis of Deposits.*—After drying and weighing, these were wrapped in a further quantity of lead foil and sufficient silver added to

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give a parting mixture. After cupellation and treatment with acid the residual gold was washed on to a small filter, and after roughly drying, this was again enclosed in a minimum of lead foil and cupelled.

(5) *Composition of Deposits.*—Following the method referred to in previous papers the composition of the alloy may, under exceptional circumstances, be obtained by a comparison of its weight with that of the copper deposited in the coulomb meter. Thus if deposition is quantitative, that is, strictly proportional to the chemical equivalents, the relation of the weight of the extreme alloy containing only gold to that of "sulphate," copper will be as 197 : 31·8 or as 6·195 : 1, while with the oppositely extreme alloy free from gold, the proportion will become 108 : 31·8 or as 3·396 : 1. Between these extremes each intermediate proportion corresponds to a definite composition of alloy as may be seen from the following table :—

TABLE II.

Composition of Alloy.		$R = \frac{\text{Weight Deposited Alloy}}{\text{Copper from Meter}}$.
Per Cent. Gold.	Per Cent. Silver.	
100	0	6·195
90	10	5·72
80	20	5·32
70	30	4·97
60	40	4·66
50	50	4·39
40	60	4·14
30	70	3·93
20	80	3·736
10	90	3·557
0	100	3·396

These values are plotted in the accompanying curve (Fig. 1) and from the curve or figures the following expressions are obtained for calculating the percentages of gold or silver for any given value of R.

$$\text{Per cent. gold in deposit} = \frac{221}{R}(R - 3{\cdot}396).$$

$$\text{Per cent. silver in deposit} = \frac{121{\cdot}5}{R}(6{\cdot}195 - R).$$

These calculated values, however, can only be true when hydrogen is not deposited, but in the case of simultaneous evolution of the gas they represent limits which, in the case of gold are minima, and with silver, cannot be exceeded.

Effect of Current Density.

For these experiments the solution contained—

Gold	14·4 grams per litre
Silver	7·2 „ „
Free cyanide	negligible.

Solution at room temperature and stirred. The results are embodied in Table III. and the variation of gold per cent. with current density is clearly seen in curve A Fig. 2. The anticipated increase in the propor-

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TABLE III.

See Fig. 2, Curve A.

Solution
Gold, 14·4 grms. per litre.
Silver, 7·2 ,, ,, ,,

Temperature of solution = 20° C.
Solution stirred.

Experiment.	C.	P.D.	Copper from Coulomb meter.	Weight Alloy Deposited.	R.	Percentage Gold.		Per Cent. Current Depositing.		Remarks on Deposits.
						Calc.	Found.	Gold.	Silver.	
1	·31	2·15	·1232	·4363	3·549	10·15	15·93	9·1	87·5	White. No trace of yellow.
2	·41	2·40	·1216	·4335	3·565	10·5	18·02	10·35	86·1	Faint tinge of yellow.
3	·515	3·15	·1524	·6138	4·028	34·7	40·01	26·0	71·2	Yellow deposit slightly burned.
4	·62	3·80	·1226	·5035	4·107	38·3	47·35	31·4	63·6	Darker.
5	·81	4·0	·1589	·6537	4·114	38·6	57·90	34·5	58·3	Rough dark deposit.

TABLE IV.

See Fig. 2, Curve B.

Solution
As in Table III.

Temperature of solution = 50° C.
Solution stirred.

Experiment.	C.	P.D.	Copper from Coulomb meter.	Weight Alloy Deposited.	R.	Percentage Gold.		Per Cent. Current Depositing.		Remarks on Deposits.
						Calc.	Found.	Gold.	Silver.	
1	·52	2·20	·1023	·3556	3·476	5·2	16·31	9·15	85·5	White. No trace of yellow.
2	·62	2·40	·1233	·4459	3·616	13·5	18·86	11·0	86·3	Good deposit; trace of yellow.
3	·65	2·75	·1282	·5104	3·981	32·4	38·56	24·8	72·0	Uniform light yellow deposit.
4	·706	2·95	·1389	·5796	4·173	41·7	45·67	30·7	66·8	Light yellow deposit.
5	·802	3·15	·1580	·6752	4·272	45·3	45·20	31·2	68·8	Dark yellow deposit.
6	1·02	3·40	·1603	·6476	4·04	35·2	48·75	31·8	61·0	Dark yellow and rough.

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tion of the more positive gold is forthcoming, though the rate of deposition is far in excess of that which would ordinarily be employed in the gilding process, amounting, in experiment 5, to as much as 40 amperes per square foot.

Effect of Temperature.

The temperature of the solution was raised to 50° C. and the stirring continued. A similar series of experiments was made and the results are given in Table IV. Here the P.D.'s required to maintain the same current densities are markedly less and the percentage of gold is thereby considerably diminished, this being very obvious when comparing

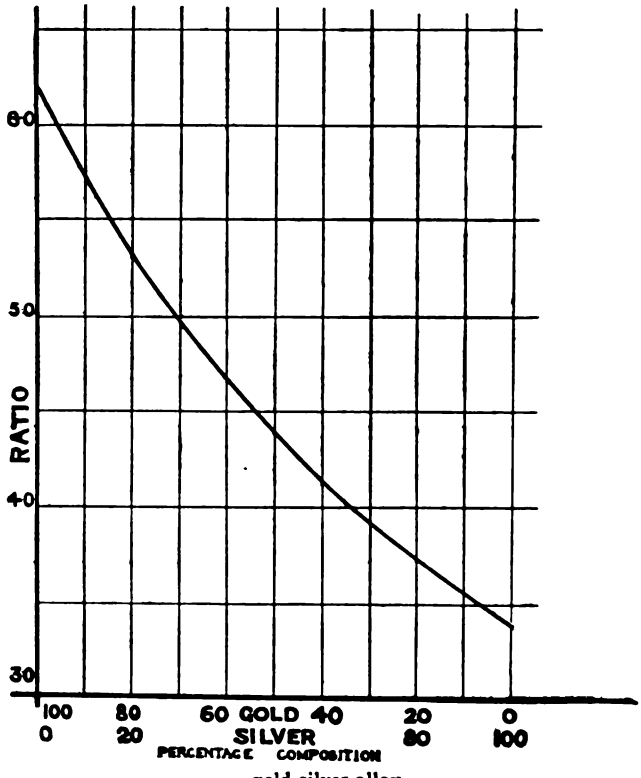

Fig. 1.—Relation of ratio $\frac{\text{gold-silver alloy}}{\text{copper from sulphate}}$ to composition of alloy.

curves A (cold) and B (warm) in Fig. 2. On the whole the conditions are favourable to quantitative deposition of the metal, this being seen from the addition of the percentages in the last two columns, in one case (experiment 5) no hydrogen appearing at all. It may perhaps be explained here that the percentage of current depositing silver is calculated from the difference in the weight of the deposit and that of the gold which it is found to contain.

Effect of Concentration.

A portion of the solution was then diluted with its own volume of water and a further series of deposits made under otherwise similar conditions,

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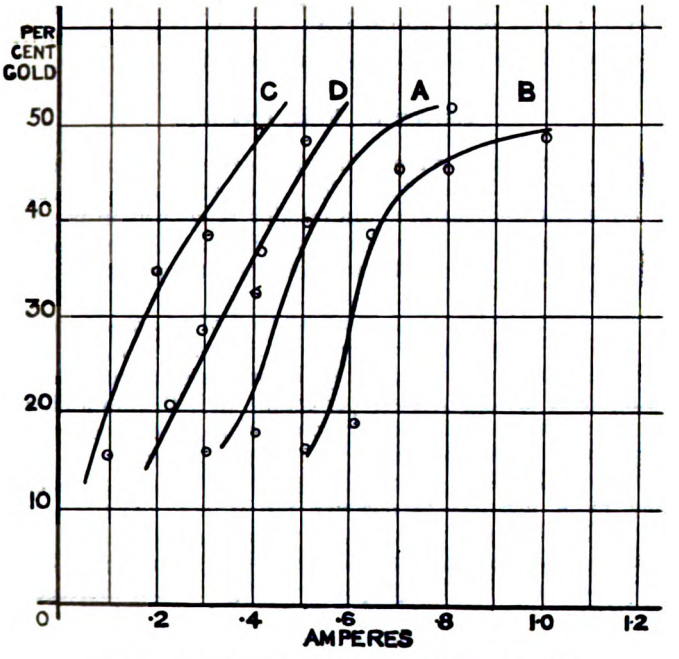

FIG. 2.—Effect of current density and concentration.

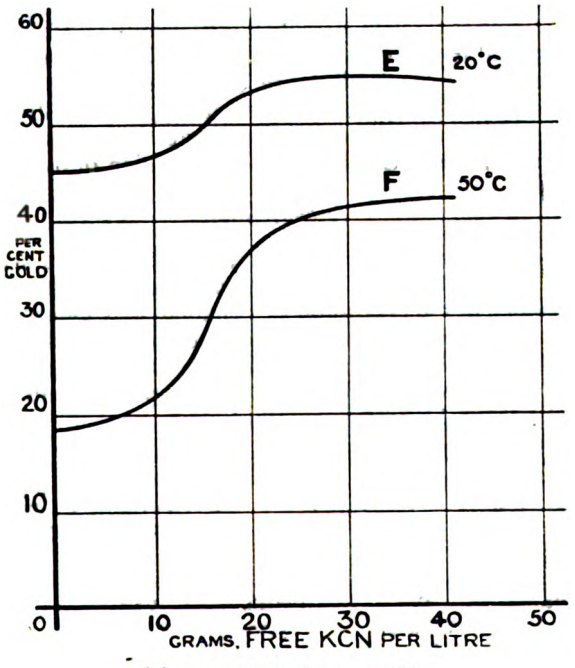

FIG. 3.—Effect of free cyanide.

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using the solution both cold and warm. The results are embodied in curves C and D in Fig. 2 which indicate an increased proportion of the more positive gold in both cold and warm solutions.

Effect of Free Cyanide.

It now remained to find the influence of excess of potassium cyanide on the composition of the resulting alloy. For this purpose successive additions of the salt were made to the solution previously in use to bring up the content to 10, 20, 30, and 40 grams per litre. Experiments were then conducted with both cold and warm solutions, the results being indicated in curves E and F in Fig. 3.

In these experiments a constant current of ·3 ampere was aimed at corresponding to ·08865 gram of copper in the coulomb meter. Variations from this figure were small and except in one case did not exceed 1·3 per cent. being more usually below 1 per cent. In both cold and warm solutions free cyanide raises the proportion of gold in the deposit, the effect being apparently more pronounced in the warm solution.

Summary of Results.—Thus while gold is in many of its compounds decidedly more negative than silver, the cyanide solutions provide an exception. The figures for the single potentials of gold and silver given on p. 502 in potassium cyanide solutions are confirmed by:—

1. The increase in the proportion of gold with increased current density.
2. The decrease in the proportion of gold with increased temperature.
3. The larger proportion of gold obtained from more dilute solutions.
4. When however we trace the effect of free cyanide it is found that—

(*a*) There is a quantitative improvement of the deposit with increasing cyanide, but

(*b*) In spite of the lowering of P.D. with additions of free cyanide the proportion of gold increases, indicative of a smaller difference between the two metals as shown by the increase of the percentage of gold without change of other conditions. In the case of copper zinc alloys the reverse occurs, the addition of cyanide inducing a greater difference between the two metals and thus facilitating the easier separation of the copper.

Supplemental.

In order to supplement the work an attempt has been made to obtain a number of similar deposits during the course of the routine work of one whose experience of the deposition of coloured gold deposits is far wider than that of the author. A series of three weighed lead cathodes was supplied, and from the ordinary solution in constant use deposits were made with varying current densities. The plates were returned for analysis and yielded the following results:—

Solution used:—

Gold 8 dwts.	Equivalent to	2·74 gms.
Silver 1½ ,,		·43 ,,
KCN. 8 ozs.		50 ,,
Water 1 gallon		1 litre

No. of Plate.	C.	Weight of Deposit.	Weight of Gold.	Per cent. Gold.
1	·25 amp.	·3420	·2664	77·9
2	·75 ,,	·5300	·4120	77·7
3	1·25 ,,	·3614	·2774	76·7

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Comparing these results with those obtained on the laboratory scale the higher percentage of gold is readily accounted for by—

1. the larger proportion of gold to silver, *viz.*, 6 : 1,
2. the more dilute solution,
3. the relatively large proportion of free cyanide.

The author of these experiments, reports without any idea of the composition of his deposits that he finds very little variation in the shade of the deposit with varying current density. Variations in shade arise mainly owing to the loss of silver from the bath. A small silver anode is used side by side with a larger gold plate but no control over the corrosion of the two plates and consequently of the composition of the solution can be effected apart from a knowledge of the respective amounts of gold and silver passing out into the deposits.

With the preponderance of free cyanide common to ordinary plating solutions the conditions of deposition become much more uniform and thus capable of more easy control.

The author acknowledges with gratitude the able assistance rendered by Mr. T. Johnson in carrying out the assays of the many deposits which have been made.

Electro-chemical Laboratory,
Northampton Polytechnic Institute,
London, E.C. 1.

DISCUSSION.

Mr. E. A. Smith: There is one industrial application with regard to the deposition of these triple alloys of gold, silver and copper. For many years the Americans have been trying to use the simultaneous electrodeposition of silver, copper and gold for the production of artificial dentures in dentistry. Most of these have failed because of the difficulty of maintaining a deposit of regular composition ; it was found to vary from the beginning to the end of the process. Then also the deposited metal was inclined to be brittle, or at any rate not sufficiently elastic to withstand the wear and tear to which artificial dentures are subjected. But quite a fair amount of experimental work has been done in the deposition of these triple alloys though I think I am correct in saying that no very successful results of industrial importance have so far been obtained. I am sure that the figures Mr. Field has put before us will be of interest and will add to the data we have already in connection with the deposition of triple metals.

Mr. J. N. Greenwood: There seems to be just one feature in this simultaneous deposition of three metals which is rather important in view of what occurred early in the afternoon—the question whether the two metals are deposited in solid or whether they are deposited separately whilst being an atomic mixture or not truly in solution. It happens to be a question of getting deposits which are considerably harder than either of the two component metals. If the deposit is a true solid solution it seems to open up a field for these stiffer deposits which I take it are necessary in a good many articles of commerce.

Dr. E. B. R. Prideaux: There is one point which is perhaps of less importance to the practical electroplater but interests people on the educational side. In his earlier paper on the electrodeposition of brass Mr. Field made some attempt to calculate the potential. I should like to ask whether he has

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made any similar attempt in the case of silver and gold, and also whether he has done what is perhaps more practical: whether he has tried to measure the single potentials of silver and gold in the cyanide solutions which he used.

Mr. S. Field replied as follows to the discussion: The data used emanated from a paper by Christie read before the American Institute of Mining Engineers, and the figures given this afternoon are from the same source. It is a point which bears rather closely upon this matter. I have no experience of the photo-micrographic examination of these deposits. Of course the deposits were quite small and were consumed in being analysed, but it always appeared to me that such deposits would be solid solutions; practically the equivalent of the metal when cast.

The **Chairman**: I think it may be taken that these deposits are always solid solutions. A good deal of work has been done in Vienna by Kramer, who has published a number of papers on the deposition of alloys, and the evidence shows clearly that they always are solid solutions.

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Mr. W. E. Hughes, B.A., presented a paper on "The Use of Colloids in the Electrodeposition of Metals," which in the absence of the author was taken as read. The following is an abstract of the paper, which is printed in full in the Report of the General Discussion on "The Physics and Chemistry of Colloids" held by the Faraday Society and the Physical Society of London on October 25th, 1920 [See Appendix to this vol.].

Colloids and substances producing the same effects were often usefully employed in electroplating solutions. In one case at least—that of lead—no coherent deposit could be obtained unless some colloid, for instance, glue or peptone, was used. The effect usually produced by the colloid addition was a diminution of the size of grain of which the deposit consists, the diminution being, in some cases, so extreme that, to the naked eye, the deposit appears plastic and non-crystalline. The mechanism of the change from macro-crystalline to micro-crystalline was unknown. The differing views of Marc, Kohlschütter, and Freundlich and Fischer were referred to, and it was suggested that this difference of opinion was in itself sufficient reason for drawing attention to the operation of colloids in plating solutions, which was of interest both practically and theoretically.

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Papers and Discussion on "Electroplating".

The Evening Session was devoted to the reading and discussion of papers on "Electroplating".

Mr. E. A. Smith presided.

The **Chairman**, in opening the preceedings, said: The particular subject we are discussing here to-night is the electrodeposition of silver, and we are reminded that one of the functions of the Faraday Society is to deal with subjects such as electroplating which are described as "borderland" subjects, the full consideration of which involves the bringing together of men engaged not only in the purely scientific side but also those concerned in the technical side of the subject. I think no better centre could have been selected for dealing with the electrodeposition of silver than Sheffield. This city has a record of nearly 160 years in the electrodeposition of silver, and during that period considerable developments have been made; developments which have been marked by a due regard to the application of scientific principles. In spite of what has been accomplished, and the progress that has been made, it is well for us to remind ourselves that research is an essential preliminary to progress, and if the industry is to be kept efficient and up to date it is necessary for all engaged in it to be conversant with the latest scientific work in connection with electroplating. We therefore welcome to-night three or four very important papers which deal with the scientific work which has been done recently, and we hope, as a result of this meeting, and the discussion which will take place, that many connected with the electroplating industry of this city and elsewhere will derive considerable benefit and help for their work. Without further remarks, I have pleasure in calling upon Mr. W. R. Barclay to read his paper on "Electro-Silver Plating and its Technical Development".

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ELECTRO-SILVER PLATING.

PART I. EARLY TECHNICAL HISTORY.

PART II. THE AUTHOR'S INVESTIGATIONS.

BY W. R. BARCLAY, O.B.E., A.M.I.E.E.

PART I.

The purpose of this paper is to present a brief summary of the technical development of electro-silver plating together with a survey of our present knowledge of the subject and the investigations still needed to deal adequately with its problems.

The recent publication of a paper by Mr. R. E. Leader[1] has placed on record a really authoritative account of the discovery by Wright, in 1840, of the cyanide solutions which form the basis of all industrial silver plating, and the introduction of the resulting processes into commercial practice by the Elkingtons.

But apart from a number of patent specifications—most of them valueless—relatively little systematic investigation of the varied phenomena of silver plating practice is to be found in literature until towards the end of the nineteenth and beginning of the twentieth century.

It may be said indeed that not until the pioneer work of Hittorf, Ostwald, Arrhenius, Haber, and others had laid the foundation of the modern science of electrochemistry, was any adequate scientific survey of the subject possible.

In spite of this, however, we owe more than perhaps is readily understood to a few workers of the nineteenth century.

Messrs. Glassford and Napier in 1844 investigated the chemistry of the double cyanides, and threw considerable light on the reactions involved in making up the plating bath.

Smee, in 1843, published the second edition of his "Elements of Electro-metallurgy"—the first scientific treatise on the subject. This revised edition is well worth the study of electroplaters even now. It contains much of permanent value, and is particularly interesting in its treatment of the subject of the physical characteristics of electrodeposited metals. While taking a mistaken view of the exact influence and bearing of hydrogen liberation on deposits, Smee grasped very clearly the importance of current density; and—considering the state of electrochemical knowledge in his day—showed quite remarkable insight into the question of the relationship between metal concentration and current density.

He states, *e.g.* "to obtain with certainty any particular metallic deposit we must regulate the galvanic power actually passing to the strength of

[1] *Journ. Inst. Metals*, vol. xxii., pp. 305-26.

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the metallic solution ".[1] Farther on he says, "the quality of the metal depends on the regulation of the quantity of electricity to the strength of the metallic solution ".[2]

An interesting statement on silver deposits is the following:—

"The silver will be thrown down in somewhat different states according to circumstances. If thrown down very slowly, it will assume a beautiful dead appearance, if still more rapidly, it will be brighter."[3]

Gore, whose scientific career covered a considerable portion of the latter half of the nineteenth century, is the chief contributor on the subject to scientific and technical literature, and his position as technical adviser to the Elkingtons, and general consultant to the trade in Birmingham, entitles him to the careful attention of all workers in the art.

Even Gore, however, does not appear to have published any detailed observations bearing on practical problems, although he investigated largely the electro-chemistry of many silver compounds.

For the most part, his views are embodied in his "Art of Electro-Metallurgy" (Longmans, 1877, and subsequent editions) and his "Electro-Chemistry" (Electrician Publishing Company, 1887), both of which works are still available in libraries.

Another author of the same period deserving at least brief mention is Dr. Georg Langbein, the first edition of whose "Vollständiges Handbuch der Galvanischen Metall-niederschläge," appeared in 1886. Langbein, however, contributes little of importance, except to be more definite than his contemporaries in giving exact values of current density and E.M.F., as also in stating the relative proportion of free cyanide to be recommended for practical work. On the other hand, it must be said that he is a little misleading in some respects, as *e.g.* in his references to the use of carbon bisulphide in "bright" plating vats.[4]

It was not until the early part of the present century that any really systematic investigations into the various factors of technical importance began to appear in scientific and technical journals.

The period 1900-1910 is much more prolific than any other in the history of the art in this direction, and during these years work of first-rate importance has been published.

In 1904 Bancroft[5] published a paper of considerable interest entitled "The Chemistry of Electro-Plating," in which a number of problems awaiting solution were discussed. Amongst these was the question of the exact cause of the variation in the structure of deposited metals when varying current densities were employed. Bancroft put forward the interesting explanation that the structure of metals deposited by high current densities was exactly analogous to the structure of precipitates produced rapidly by purely chemical reactions. This view has been widely endorsed,[6] and is of importance as rendering intelligible at least in some degree the widely varying physical structures of deposits it is possible to obtain from identical solutions.

Of still more importance, however, was the publication by Brunner in Germany in 1907 of his "Beiträge zur Kenntnis der Elektrolytischen Abscheidung der Metalle," Dresden.

[1] "Elements of Electro-Metallurgy," 2nd edit., 1843, p. 114.
[2] *Ibid.*, p. 127.
[3] *Ibid.*, p. 217.
[4] Langbein, "Vollständiges Handbuch der Galvanischen Metallniederschläge". Leipzig, 1886, p. 179.
[5] *Trans. Amer. Electrochem. Soc.*, 1904, pp. 27-43.
[6] See Miller, *Trans. Amer. Electrochem. Soc.*, 1913, vol. xxiii., p. 18.

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This work deserves extended reference, particularly since so far as the present author's knowledge goes, it has not been translated into English and (probably in consequence) has received comparatively little attention in this country.

Brunner investigated (*inter alia*) the influence of current density, potassium cyanide, and metallic silver content, on the efficiency of silver cyanide electrolytes, and the physical characteristics of resulting deposits.

The practical value of his work must be the apology for including some of his results in the present paper, as in the accompanying Tables.

Tables I, II, III, XI, XII, are of experiments carried out in an atmosphere of hydrogen, while those of IV, V, VI, VII, VIII, IX, X, XIII, XIV, XV and XVI are in air.

The scientific conclusions which have been based on these experiments, particularly on the comparisons of the results in hydrogen and air respectively, have been discussed fully by Brunner himself, as also by Schlotter.[1] They show clearly that even with a solution of very low silver content there is little tendency to hydrogen liberation, except at very high current densities, and that the small loss in cathode efficiency is largely due to the depolarisation of hydrogen ions (on discharge) by dissolved air.

From the point of view of the practical silver plater, these figures reveal the extraordinary latitude allowable in the relationship of the three main factors of practice, *viz.*: "current density," "metal concentration," and "free cyanide," and yet indicate unmistakably what may be termed "the path of safety".

With regard to these factors it may be observed—

(1) As to current density—how significant is the figure of 0·003 amperes per sq. cm. (approx. 2·75 amps. per sq. ft.). In each of the experimental series, in spite of solutions widely different in composition, a C.D. of this value gives not only a very high (in many cases 100 per cent.) efficiency but—with the exception of the extreme conditions in Tables XIV, XV, and XVI—a satisfactory deposit.

It must, however, be noted that these are laboratory experiments.

(2) As to metal concentration and free cyanide, it will be seen that the best results are obtained when the relationship between the double salt $KAg(CN)_2$ to free KCN content is practically a molecular ratio of 1 : 2.

(3) The value of agitation in working silver-plating baths is shown throughout the series, but remarkably emphasised by the results embodied in Tables XV and XVI as also VIII, IX, and X.

This work of Brunner (as also Foerster[2]) has placed our knowledge of the foregoing factors of silver-plating practice on a sound foundation which cumulative practical experience has on the whole amply confirmed.

Part II.

In 1904 it fell to the lot of the present author to attempt the co-ordination of the working of two electro-silver plating plants of widely different origin and different working conditions.

The difficulties encountered led him to undertake on a practical scale a careful comparison of the working of silver vats, with widely varying proportions of both "silver" and "free cyanide" content.

[1] *Galvanostogie I Teil über Elektrolytische Metallniederschläge*, 1910, pp. 142-48.
[2] *Zeits. Elektrochem.*, 13, 561 (1907).

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In the two plants referred to were vats with a silver content from as low as 20 or 22 dwt. per gallon (6 to 7 grams per litre) to as high as between 5 and 6 oz. per gallon (30 to 35 grams per litre). The free cyanide content also varied from 14 per cent. to approximately 100 per cent. of the combined cyanide.[1]

Some of these solutions were upwards of forty years old, while others were less than five years old.

Observations of the behaviour of these were carried on over a period of approximately three years, and the general conclusions arrived at may be summarised as follows:—

The best results were obtained—

(*a*) In general, from old solutions.

(*b*) From solutions containing over 2 oz. but not more than 4½ oz. silver per gallon.

(*c*) From solutions where the percentage of "free" KCN to "combined" KCN was from 75 per cent. to 100 per cent.

(*d*) From solutions in regular use rather than from those intermittently used.

(*e*) Where the temperature of the vats was not less than 17° C.

Since the exact data on which these conclusions were based cannot—for obvious reasons—be given, some further explanation is necessary, but first the question must be discussed.

"What constitutes a good result in commercial silver plating?"

The main factors, leaving out "adhesion" which is largely a matter of basis metal and preparation—are undoubtedly

(1) A perfectly smooth, finely grained, and lustrous deposit, relatively soft and capable of being readily burnished and polished.

(2) Rapid deposition, *i.e.* high electrolytic conductivity.

(3) A high anodic and cathodic efficiency.

Now with regard to the conclusions outlined above, it will be observed (leaving (*a*) for the moment) that (*b*) is in accordance with recent general investigations into the subject of the electro-deposition of metals, which have shown that a high metallic concentration is an essential to rapid deposition and thick deposits.[2] On the other hand the experience not only of the author but many practical platers has shown that when the silver content of a vat appreciably exceeds 4 to 5 oz. the solution becomes sluggish and difficult to work, and is very liable to yield irregular deposits (probably owing to an aptitude to settle into layers of varying density).

In any event such solutions are financially uneconomic.

(*c*) is confirmed very closely by the laboratory experiments of Brunner, and is still further endorsed by the experience of many Sheffield electro-platers, who have been good enough to furnish the author with the results of their own work.

Some explanation may be necessary as to this method of calculating free cyanide as a ratio of the combined cyanide. From a practical point of view it is distinctly advisable to correlate these factors, but it must be pointed out that the necessity for definite proportions of free cyanide is influenced by the factor of C.D., inasmuch as one of the chief functions

[1] These percentage figures are based on the percentage of "free" to "combined" cyanide, the latter being calculated on the equation. Agx + 2KCN, x being, of course, an univalent radicle.

[2] See, *e.g.*, Pring and Tainton on Zinc, *Trans. Chem. Soc.*, 1914, vol. cv., p. 710; Kalmus, Harper, and Savell on Cobalt, *Jour. Ind. and Eng. Chem.*, 1915, 7, p. 379; Watts on Nickel, *Trans. Amer. Electrochem. Soc.*, 1916, vol. xxix., p. 395.

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of free cyanide is to dissolve the AgCN formed at the anode as the result of the decomposition of the complex anion $Ag(CN)_2$—which is obviously quantitatively determined by the C.D. employed.

From a purely theoretical point of view conclusion (*d*) is a little difficult to understand, and the author hesitates to advance any explanation, though his experience is confirmed by other workers. It is indeed a truism in silver-plating practice that "the more a solution is worked the better it becomes".

This subject has been investigated by Jordis and Stramer[1] who conclude (*inter alia*) that the content of carbonates increased more rapidly in used baths than in similar baths not regularly used. These authors also found that ammonia, ammonium cyanide, and potassium formate are present in old and used baths.

This point is, however, somewhat akin to conclusion (*a*) which must now be dealt with more fully. Not only in the particular observations now referred to, but from many sources evidence is forthcoming of the undoubted superiority of old solutions over new ones.

Most writers on electroplating who have referred to this point (notably Langbein and McMillan) have attributed the improvement to the gradual accumulation of organic matter which undoubtedly occurs.

That it is a question of the presence of substances other than $KAg(CN)_2$ and KCN is evident when vats of almost identical silver and free cyanide content are compared under conditions of equal temperature and current densities. The older vats in general show a higher conductivity and yield a more lustrous and consequently more easily polished deposit. Practical experience, however, has demonstrated that this explanation is not fully adequate.

Chemical examination of a number of these old solutions (forty to sixty years) reveals the presence of surprisingly large amounts of potassium or sodium salts other than cyanide.

The author has previously published[2] an analysis of such a solution which may be regarded as typical, and through the kindness of Mr. Arthur Bowker he has recently had the opportunity of examining another old Sheffield solution, which has been in regular use for approximately sixty years.

In this instance the total solid matter present was very high indeed, being approximately 179 grams per litre of which an appreciable proportion appeared to be organic.

Time and facilities have not admitted of a complete analysis being carried out, but the following have been determined:—

Potassium Silver Cyanide	$(KAg(Cn)_2)$	. .	26·63 grams per litre
Potassium Cyanide	(KCN)	. .	16·04 ,, ,, ,,
Carbonates	(as K_2CO_3)	. .	21·37 ,, ,, ,,
Chlorides	(as KCl)	. .	20·8 ,, ,, ,,

It will be noted that the content of chloride is an important item in the composition of this solution, and is undoubtedly due to the practice of some of the older platers of making up their baths from silver chloride.

The question of the presence of potassium salts, other than cyanide, in silver-plating vats has been the subject of comment (usually adverse) by most writers on electrodeposition. Particularly has the presence of

[1] *Zeits. Elektrochem.*, 1903, **9**, s. 572.

[2] Barclay and Hainsworth, "Electroplating". Arnold, 1912, p. 193.

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potassium chloride been condemned by such authorities as Sprague,[1] Gore,[2] McMillan,[3] and others. One of the very few exceptions is Langbein who quite properly points out, what the others apparently ignore, that its presence increases the conductivity of the bath. This would be expected from purely theoretical considerations, but the point is established beyond question by the work of Frary and Porter,[4] who found that both the "chloride and hydroxide have a decided effect in increasing the conductivity," both having apparently the same value as an equivalent "free cyanide" content. This paper (by Frary and Porter) is of great interest as representing a systematic attack on the problems of this subject of the complex composition of commercial silver-plating baths. These workers investigated mainly the influence of the presence of potassium chloride or potassium hydroxide on the simple potentials of various metals usually used as cathodes in silver plating, *e.g.* mercury, silver, copper, brass, iron, and zinc. As previously indicated the specific conductivity of the various electrolytes was also determined. The investigations show clearly that no appreciable difference results from the presence of KCl or KOH on the electrode potentials, and that therefore no adverse effects in adhesion of deposits need be feared. The interesting statement is made "that the specific gravity of the solution may be regarded as a rough measure of its conductivity". This is in general accord with the author's practical experience.

The general conclusions which the author has reached as the result of co-ordinating his own experience with that of many other workers in the same field, may be summarised as follows:—

(1) That the most suitable silver content of an electrolyte for commercial silver plating, having regard not only to technical efficiency but to economic considerations, is approximately 3 troy oz. per gallon (22 to 25 grams per litre).

(2) That the proportion of free potassium cyanide in such a solution should follow the molecular ratio—

$$KAg(CN)_2 : 2KCN.$$

Thus the composition of the electrolyte recommended would be—

Potassium Silver Cyanide, $KAg(CN)_2$.	$5\frac{1}{2}$ troy oz. or 38 grams
Potassium Cyanide, KCN . . .	$3\frac{1}{2}$ „ „ 24 „
Water	1 gallon or 1 litre.

(3) That the presence of such potassium salts as the hydrate, carbonate, chloride, and cyanate are advantageous, at least within such limits as obtain in normal silver-plating practice in the case of solutions in regular use for relatively long periods of time (thirty to forty years); and that therefore new solutions may be made from the corresponding silver salts without fear of untoward results.

(4) That a factor of vital importance in commercial practice is *current density*, it being essential that this factor be correlated to the metallic strength of the solution and the proportion of free cyanide employed. Thus, for example, a low current density yielding good results from a solution of silver and potassium cyanide of, say, 1 oz. per gallon, would be too low for such a bath as recommended above. Not only would the work be slower in operation, but the physical quality of the deposit would

[1] "Electricity," 2nd ed. Spon, 1884, p. 420.
[2] "Art of Electro-Metallurgy." Longmans, 1887, p. 159.
[3] "Treatise on Electro-Metallurgy," 2nd ed. Griffin, 1890, p. 198.
[4] *Trans. Amer. Electrochem. Soc.*, 1916, vol. xxviii, p. 323.

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suffer. A current density of 2¾ to 3 amperes per square foot is, however, suitable over a very wide range of bath compositions.

(5) That the working temperature of silver-plating baths is also important and should vary within limits not greater than 17° C. to 23° C.

(6) That a regular addition of potassium cyanide should be made weekly to a bath in regular use, the exact amount being regulated to that just sufficient to keep the free cyanide content to the standard given above. In vats containing 150 gallons, this will probably amount to not more than 1 lb. per week.

(7) That commercial plating baths should be used regularly (and not intermittently), under the same conditions of current density.

Finally it may be pointed out that while the present technical position of the art has reached a high level of efficiency, and a number of important problems have been satisfactorily solved, a considerable field of research is still open on such questions as—

(*a*) The exact influence of organic matter on the physical structure of the deposit.

(*b*) The chemical and electrochemical reactions occurring during the electrolysis of industrial silver-plating baths, and particularly of those complex solutions of considerable age which are found in practice to give such excellent results.

The author desires to acknowledge his indebtedness to Mr. R. G. Johnstone of the Midland Labaratory Guild for valued assistance in chemical analysis, etc., also to Dr. Schlotter's "Galvanostogie über Elekrrolytische Niederschläge," from which he has extracted the figures relating to Brunner's experiments, p. .

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Table.	Condition of Atmosphere.	Composition, grams per litre. AgCN.	KCN.	Current Density, per sq. cm.	Cathode Efficiency, per cent.	Mean Bath Tension, volts.	Character of the Silver Deposit and Observations.
I	Hydrogen with stirring	13·4	8·125	0·001	99·66	0·44	Unsatisfactory deposit.
				0·002	90·33 / 98·26	irregular	Unequal stirring.
				0·003	99·66	0·83	
				0·004	94·07 / 96·13	2-3	Separation of AgCN on anode.
				0·005	95·18	3·8-4·5	
II	Hydrogen with stirring	13·4	19·5	0·001	99·68 / 99·28 / 99·41	0·14-0·26	Matt, white, somewhat lustrous.
				0·002	99·31 / 99·85	0·29-0·35 / 0·4	Lustrous. ,,
				0·003	100	0·37-0·45	Partially lustrous.
				0·005	100 / 99·9	0·5-0·8	,, ,,
				0·01	98·1	1·5-1·6	Matt, powdery on edges.
III	Hydrogen with stirring	13·4	65	0·001	99·8	0·12-0·14	Very fine deposit.
				0·002	99·8	0·24	Very fine deposit, somewhat lustrous.
				0·003	100	0·35-0·32	Very fine deposit, somewhat lustrous.
				0·004	99·67	0·4	Very fine deposit, somewhat lustrous.
				0·005	99·64 / 99·52	0·48-0·5	Very fine deposit, somewhat lustrous.
IV	Air with stirring	13·4	8·125	0·001	83·09	0·4	Matt, white.
				0·002	89·01	1·1·6	
				0·003	92·64	0·8	
				0·004	93·5	over 5	AgCN on anode.
V	,, ,, ,,	13·4	19·5	0·001	81·86 / 96·88	0·1-0·14	Matt, white, a little spongy in layers.
				0·002	89·1 / 97·59	0·24-0·28	Fine matt, steel white, somewhat lustrous.
				0·003	94·78 / 98·28	0·35 / 0·34	Very fine. Very slightly lustrous.
				0·005	97·17	0·58	Very fine, slightly lustrous.
				0·01	95·6	1·2	Matt on edge.
				0·02	94·25	2·2	Lustrous in centre.
VI	,, ,, ,,	13·4	65	0·001	90·35	0·14	Slightly lustrous.
				0·002	91·67	0·25-0·3	,, ,,
				0·003	95·8	0·32	,, ,,
				0·004	98·36	0·4	Fine matt.
				0·005	97·2	0·4-0·47	,, ,,
VII	,, ,, ,,	13·4	260	0·001	100	0·08-0·1	Lustrous.
				0·002	99·6	0·1	,,
				0·003	100	0·12	,, steely white.
				0·005	100	0·15	Slightly lustrous.
				0·01	100·3	0·26	Very fine matt.
				0·02	100·4	1·0	Powdery.
				0·04	76·03	1·2-1·4	Deposit not weighable.

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Table.	Condition of Atmosphere.	Composition, grams per litre. AgCN.	Composition, grams per litre. KCN.	Current Density, per sq. cm.	Cathode Efficiency per cent.	Mean Bath Tension, volts.	Character of the Silver Deposit and Observations.
VIII	Air without stirring	13·4	19·5	0·001	97·45	0·15-0·2	Very fine, slight lustre.
				0·002	99·21	0·3-0·4	,, ,, somewhat lustrous.
				0·003	100	0·54-0·6	Fine matt, somewhat lustrous.
				0·005	97·15		Greyish, spongy edges; gas evolved.
IX	Air without stirring	13·4	65	0·001	97·33	0·03-0·1	Matt, greyish.
				0·002	99·67	0·14-0·18	,, white.
				0·003	{99·10 / 99·37}	0·2	,, ,,
				0·005	{90·13 / 94·81}	0·8-1	Powdery grey.
				0·01	84·84	1-1·2	,, ,,
				0·02	62·7	1·5-1·6	Loose deposit.
X	Air without stirring	13·4	260	0·001	97·88	0·14-0·4	Lustrous.
				0·002	97·77	0·26-0·5	,,
				0·003	99·27	0·38-0·46	,,
				0·005	91·89	0·8-0·88	Matt; gas evolved.
				0·01	87·4	1·0-1·4	Spongy; gas evolved.
				0·02	73·31	1·2	,, ,, ,,
XI	Hydrogen with stirring	4·5	19·5	0·001	100	0·12-0·2	Matt.
				0·002	100·14	0·37	,,
				0·003	99·66	0·44-0·5	,,
				0·005	99·63	0·76-1·0	,,
				0·01	99·2	1·26-1·34	Matt; somewhat spongy.
				0·02	83·2	2·7	Spongy.
XII	Hydrogen with stirring	1·34	19·5	0·001	97·87	0·15-0·2	White.
				0·002	{98·83 / 97·76}	0·5-0·62	,,
				0·003	91·12	0·6-0·7	,,
			–	0·005	57·99	1·2	Spongy; gas evolved.
XIII	Air with stirring	4·5	19·5	0·001	92·44	0·13	Slightly lustrous.
				0·002	94·21	0·2	,, ,,
				0·003	94·54	0·42	Matt.
				0·005	{95·55 / 93·83}	0·6-0·68	,,
				0·01	95·93	1·2-1·5	Somewhat spongy.
				0·02	90·69	2·2	Spongy; gas evolved.
XIV	,, ,, ,,	1·34	19·5	0·001	89·47	0·15-0·23	Slightly lustrous.
				0·002	93·58	0·35-0·6	,, ,,
				0·003	81·00	0·8-0·84	Grey, matt; gas evolved.
				0·005	61·17	1·5	Spongy; ,, ,,
XV	Air without stirring	4·5	19·5	0·001	97·06	0·2-0·4	Matt.
				0·002	85·42	0·88	Grey; slight evolution of gas.
				0·003	76·50	0·96	Grey; slight evolution of gas.
XVI	Air without stirring	1·34	19·5	0·001	82·29	0·68-0·7	Grey; gas evolved.
				0·002	79·97	0·8-0·9	Somewhat spongy; gas evolved slightly.
				0·003	71·15	1·8	Very spongy; gas evolved.

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THE CHEMICAL COMPOSITION OF OLD SILVER-PLATING SOLUTIONS.

WITH OBSERVATIONS ON THEIR WORKING PROPERTIES.

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AND

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Amongst practical silver-platers it is generally held that *old* silver-plating solutions have superior working qualities to similar solutions freshly prepared. Theoretically one would think that the opposite would obtain, since the impurities accumulating from decomposition during a period of years, and the presence of a number of metallic and organic compounds other than the essential silver cyanide, might reasonably be expected to be disadvantageous than otherwise.

In view of this general opinion the authors have been enabled, by the kindness of the trade platers and manufacturers of Sheffield, to examine a large number of such solutions, the majority of which have been in use for periods varying from ten to fifty years. For comparison a few have been examined which have been made during the last twelve months.

The examination of so large a number of samples as those carried out—fifty-six—is in itself a very considerable undertaking, and had more time been available it was hoped to supply figures for those rarer impurities not hitherto attempted, *viz.* cyanates, thiocyanates, etc. This, however, may be contributed at a later date, and in this paper the authors have concentrated upon the physical and electrical properties, and the cyanide, silver, and carbonate content. In presenting the paper in its incomplete form, the authors feel that the information so far gained will add materially to that already available, and speed up research in this valuable, wide, and as yet but slightly explored field.

The value of the results is enhanced since the fifty-six samples are representative of the whole of the trade of Sheffield—trade platers and private firms alike, with only two exceptions. They were samples selected from vats containing the oldest solutions in use at the present time, and in Table I will be found the age and working properties of each solution in actual works practice. It should be pointed out, however, that, in a period of twenty or thirty years, during the process of cleaning out the vats and filtering the solutions, a certain amount of admixture may have taken place. But on the whole the figures given represents, at any rate relatively, the actual years the solution has been in daily use.

A comparison of Tables I and II shows in the majority of cases a striking confirmation of the views of the plater or the age of the solution when the analytical or electrical data are carefully considered.

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TABLE I.

T = Trade plater. B = "bright" plating solution.
P = Private firm. D = "dead" deposit.

Mark.	Age (Years).		Working Properties of Solution in Actual Use.
T 1	15	B	Most satisfactory. High conductivity. Very susceptible to temperature changes. Used for "Bright" plating. Anodes tend to blacken.
T 2	32	D	Fine smooth deposit. High conductivity. Anodes white and sparkling. No tendency to rough crystalline deposit, even after many hours.
T 3	20	D	Suitable for light deposits. If current density increased deposit becomes *black*. Low conductivity.
T 4	0·5	D	New solution; smooth bluish-gray deposit, not suitable for articles with soft soldered seams.
T 5	3	D	Solution prepared from "double salt cyanide" (sodium potassium cyanide). Dead matt deposit. Coarse grain and very difficult for "finishing".
T 6	30	—	Susceptible to changes of temperature. At low temperature the deposit is liable to become rough on the edges.
T 7	30	—	Deposit slow but good.
T 8	0·5	—	New solution six months ago. Works well.
P 9	25	B	Working at 4·25 amp. per sq. ft. Not so satisfactory in cold weather. If deposition proceeds beyond 90 minutes, deposit becomes *black in patches* and beyond that becomes rough.
P 10	25	D	Working at 5 amp. per sq. ft. Not susceptible to change as P 9. Deposit slightly crystalline. No blackening of cathode even after 2½ hours. Slight tendency to "burn".
P 11	25	BD	Working at 4 amp. per sq. ft. Smooth semi-bright deposit, but will not carry continuous current for more than 50 minutes, when *black powdery* substance appears on deposit. *N.B.*—The plater suggests that the blackening of the deposit in P 9 and P 11 is due to the presence of carbon disulphide present in the solution.
T 12	17	D	Working at 3·5 amp. per sq. ft. Fine dead-white dense deposit, "probably owing to *potassium carbonate*".
T 13	17	—	Working at 3-4 amp. per sq. ft. Deposit good but faintly brown. Solution probably impure due to character of goods plated.
P 14	31	—	Satisfactory deposits.
P 15	31	—	Very good deposits.
P 16	15-20	—	Fair deposits.
P 17	0·5	—	New solution. Very satisfactory.
P 18	—	—	Fair deposits.
T 19	0·5	—	Satisfactory deposits.
T 20	30	—	do.
T 21	20	—	do. but slow.
P 26	40	—	Good reguline deposit.
P 27	36	—	do. do. Can be worked above normal rate.
P 28	10	—	Fine deposit even when CD = 4 times normal.
P 29	36	—	Good deposit. Will work above normal rate.
T 30	49	B	Perfectly satisfactory.
T 31	49	D	do.
T 32	0·5	D	do.
P 33	0·5	D	Only been used for a few weeks. No addition of cyanide made since first prepared, at which time the "free KCN" was 50 per cent. of the "combined KCN". Deposit, even under microscope, was smooth, and showed no tendency to growth of individual crystals.
P 34	40	D	Gives good results. Deposits 4 oz. per hour.
P 35	30	D	Used exclusively for Britannia metal goods. Dead deposit.

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TABLE I. (*continued*).

Mark.	Age (Years).		Working Properties of Solution in Actual Use.
P 36	40	BD	Used continuously for holloware. Works best in warm weather and gives bright deposit in summer without CS_2 additions. Deposits easily 5 oz. per hour.
P 37	40	D	Good deposit. Used for spoons, etc. Deposits 4 oz. per hour.
P 38	15	—	Can be worked at high C.D. Deposit excellent. Covers soft-soldered articles very easily.
P 39	10	—	Used for Britannia metal goods. Very reliable.
P 40	20	BD	Used for holloware: gives very satisfactory deposit. Semi-bright.
P 41	8	—	High conductivity, and very reliable. Not the slightest trace of *sediment* on the plated articles.
T 42	50	—	Very old solution. This gives the best results of T 42-T 45 at the present time.
T 43	50	—	——
T 44	50	—	——
T 45	50	—	——
P 46	25	—	Works twice as quickly as P 47. Smooth deposit. Solution overworked.
P 47	25	—	Much slower than P 46. Smooth deposit. Solution overworked.
P 48	30	—	Deposit very good. Solution in first-class condition.
P 49	30	—	[1] Deposit very good. Solution works quicker than P 48. By far and away the best of the four (P 48-P 51).
P 50	30	—	Excellent solution. In good condition but not so quick.
P 51	10	—	Comparatively new solution. Not worked during 6 years of war. Only just getting to condition.
T 52	30	D	Gives good, smooth, and clear deposit.
T 53	30	B	Smooth bright deposit, especially suitable for holloware.
T 54	0·5	D	A new solution. When first prepared the deposit was coherent but strongly crystalline. The addition of more cyanide altered this, since when the deposit has been *smooth*. Anodes are dark brown during working. No tendency to burning. Solution prepared by dissolving *silver chloride* in KCN.
P 55	30	B	An old bright plating solution. Works well.
P 56	30	D	Semi-bright deposit of good quality.
P 57	2	D	Working well. Gives better results even than P 55 or P 56.
P 59	30	D	Works splendidly. Has no peculiarities. Gives a consistently smooth adhesive deposit.
P 60	30	B	Daily additions of CS_2 in methylated spirit. Does not work as satisfactorily as formerly (the plater does not state in what particular it is unsatisfactory—it cannot be conductivity, judging by Table II.—Authors' note).
P 61	7	D	Prepared as per Barclay's formula by precipitation of silver nitrate with Na_2CO_3 and solution of the "silver carbonate" in KCN. Has worked well during whole period of use.

Methods Employed.

Specific Gravity.—By Westphal balance at 15° C.

Relative Electrical Conductivity.—This was determined by an installation by Tinsley. The apparatus consisted of a metre-wire Wheatstone bridge arranged in the usual manner for the comparison of resistances, *i.e.* the resistance of a constant volume of the solution was compared with that given by a box of standard resistance coils.

The bridge was supplied with alternating current at a pressure of 3 volts derived from 200 volt-50 frequency mains, a small transformer being employed for reducing the pressure.

[1] See Conductivity Table II.—Authors.

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The balance or null-point on the bridge was determined by means of a head gear telephone, which was found to be much more sensitive than the vibration galvanometer. The average of at least two readings was taken as the true point, and in order to limit the error each determination was balanced between 49-51 cm. The accuracy was within the limits of ± 0·3 cm.

A frequency of the order 300-400 would have been much better and would have resulted in a more musical and distinctive note, serving to differentiate between the hum in the telephone due to unbalance and extraneous causes.

The solution was contained in an H-shaped stoppered cell, the electrodes being 44 × 22 mm. and 105 mm. apart. In each experiment the direction of the current was reversed in the check determination. A series of tests were carried out to see how far the *volume* of the solution affected the figure, and it was found that between 65-100 c.c. unvarying concordant results were obtained. Below 65 c.c. part of the electrode was exposed and with 35 c.c. the figure obtained was hopelessly wrong. A uniform measured volume was therefore adopted, *viz.* 70 c.c., the temperature being constant at 15·5° C.

The results are shown in Table II, and the deductions on p. .

"Free" Cyanide.—This was determined by the well-known method of Allen and consists in titrating with N/10 silver nitrate 10 c.c. of the sample, diluted with 100 c.c. water, until a faint permanent turbidity results.

Silver Content.—The process of H. C. Wright was used, in which the silver was precipitated with ammonium sulphide and the Ag_2S dissolved in nitric acid and titrated with standard potassium thiocyanate and ferric sulphate indicator (see *Proc. Sheff. Soc. of App. Met.*, 1912). The process may be recommended as a rapid and reliable one.

Potassium Carbonate.—This was determined by precipitation with barium cyanide, filtering off and washing the barium carbonate, dissolving in N/1 HCl and completion of the titration with N/1 NaOH and methyl orange.

As some workers have found difficulty with this process, perhaps the following method which the authors have found accurate and rapid will remove some of the difficulties hitherto obtaining:—

Take 5 c.c. of the sample, *immediately* add 100 c.c. boiling water, followed at once by 20 c.c. 10 per cent. $Ba(CN)_2$ reagent. Agitate and rotate, allow to stand for three minutes and add a further 5 c.c. reagent. (In no case did the authors find an additional precipitate on the further quantity of reagent being added.) Filter at once and wash four times with hot water. Test washings until quite *free from alkalinity* to sensitive smooth litmus paper.

Expedition in the early stage is the secret of success and series of ten determinations will allow each operation to follow normally with least loss of time.

The paper and precipitate are then transferred to a 6-inch porcelain dish, 20 c.c. N/1 HCl added, the paper pulped and warmed until effervescence ceases. An equal bulk of water is then added and the N/1 NaOH run in to neutrality.

The check tests gave concordant results and the authors found it possible to carry out sixteen determinations in six hours with one operator.

The results of Table II are plotted in Graphs A, B and C which follow.

Conclusions.

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TABLE II.

T = trade platers.
P = private firms.

No.	Colour.	Specific Gravity, 15°.	Relative Conductivity.[1]	Specific Conductivity in Reciprocal Ohms per Centimetre Cube.	Potassium Carbonate, Gr./100 c.c.	Silver, Oz. Troy per Gall.	Combined Cyanide (2KCN).	Free Cyanide, Oz. Troy per Gall.	Proportion of "Free" to Combined Cyanide (Combined = 100).
									Per Cent.
1. T	Orange	1·145	341	0·151	14·03	2·021	2·433	5·04	207
2. T	Deep straw	1·124	297	0·137	11·06	2·624	3·160	3·34	106
3. T	Pale orange	1·135	299	0·138	12·54	2·182	2·627	2·51	96
4. T	do.	1·120	303	0·140	9·58	1·876	2·259	4·89	216
5. T	Orange	1·125	297	0·137	9·73	2·592	3·121	9·58	307
6. T	do.	1·162	328	0·151	14·45	2·037	2·453	1·42	58
7. T	do.	1·189	476	0·219	19·28	2·053	2·472	1·82	75
8. T	Pale straw	1·065	195	0·090	4·29	3·260	3·925	2·69	69
9. P	do.	1·120	288	0·133	9·80	3·848	4·633	3·09	67
10. P	do.	1·139	399	0·184	12·42	3·188	3·838	3·59	94
11. P	Straw	1·159	352	0·163	14·54	2·616	3·150	2·68	85
12. T	do.	1·138	298	0·137	12·96	2·206	2·656	2·50	94
13. T	do.	1·120	256	0·118	10·71	2·343	2·821	1·92	68
14. P	Orange	1·100	217	0·100	9·49	1·731	2·084	1·04	50
15. P	Pale orange	1·100	283	0·130	10·61	3·743	4·507	2·53	56
16. P	Orange	1·040	247	0·114	9·85	2·004	2·413	1·68	70
17. P	Straw	1·039	105	0·048	3·48	1·747	2·103	1·19	56
18. P	Deep orange	1·140	269	0·124	14·92	1·018	2·226	1·11	90
19. T	v. Pale straw	1·024	75	0·035	1·68	1·940	2·336	0·56	24
20. T	Pale straw	1·044	128	0·059	4·73	0·636	0·766	1·38	168
21. T	Straw	1·073	185	0·085	6·90	1·111	1·338	2·80	209
26. P	do.	1·143	343	0·158	11·75	3·317	3·994	5·91	148
27. P	Deep straw	1·166	349	0·161	14·25	3·671	4·420	6·76	153
28. P	do.	1·173	338	0·156	13·54	4·395	5·292	6·83	129
29. P	Straw	1·120	297	0·137	10·00	2·512	3·024	4·56	151
30. T	Orange	1·130	299	0·138	13·94	0·805	0·969	1·49	154
31. T	Straw	1·077	217	0·100	6·41	1·682	2·025	3·52	175
32. T	Colourless	1·055	247	0·114	2·15	1·908	2·297	8·80	383
33. P	Straw	1·032	76	0·035	1·72	2·657	3·199	1·01	28
34. P	Orange	1·078	352	0·163	16·12	1·872	2·254	4·94	219
35. P	do.	1·180	354	0·165	18·08	1·505	1·812	3·79	209
36. P	do.	1·157	385	0·177	15·03	2·560	3·082	5·52	179
37. P	do.	1·156	357	0·168	14·92	2·355	2·835	3·38	119
38. P	Straw	1·149	329	0·152	13·93	4·850	5·839	2·66	46
39. P	Pale straw	1·098	222	0·102	8·80	2·946	3·547	2·03	57
40. P	Straw	1·104	259	0·119	10·22	2·922	3·518	2·07	59
41. P	do.	1·156	333	0·154	14·25	3·107	3·741	2·80	75
42. T	Med. straw	1·170	252	0·116	10·00	1·779	2·142	2·09	98
43. T	Orange	1·146	333	0·154	14·70	1·682	2·025	3·25	161
44. T	Straw	1·115	249	0·115	10·00	2·157	2·597	2·50	96
45. T	Deep straw	1·081	180	0·083	7·29	1·457	1·754	1·42	81

[1] Relative conductivity $= \frac{1}{R} \times 10^4$.

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TABLE II.—(*continued*).

No.	Colour.	Specific Gravity, 15°.	Relative Conductivity.[1]	Specific Conductivity in Reciprocal Ohms per Centimetre Cube.	Potassium Carbonate, Gr./100 c.c.	Silver, Oz. Troy per Gall.	Combined Cyanide (2KCN).	Free Cyanide, Oz. Troy per Gall.	Proportion of "Free" to Combined Cyanide (Combined = 100).
									Per Cent.
46. P	do.	1·133	246	0·113	11·64	2·133	2·568	2·47	96
47. P	do.	1·075	155	0·071	6·82	1·320	1·589	0·82	52
48. P	do.	1·209	392	0·181	20·24	2·573	3·098	2·87	93
49. P	do.	1·232	436	0·201	19·60	4·503	5·422	4·81	89
50. P	Straw	1·190	377	0·170	17·21	3·441	4·143	2·81	68
51. P	Pale straw	1·114	223	0·103	19·67	5·000	6·020	0·29	5
52. T	Deep straw	1·122	273	0·126	10·71	2·133	2·568	2·30	89
53. T	Orange	1·132	300	0·138	13·16	2·149	2·587	1·80	69
				0·058					
54. T	Colourless	1·050	125	0·106	2·48	3·397	4·090	2·36	58
55. P	Pale straw	1·095	230	0·159	7·75	2·230	2·685	1·75	65
56. P	Straw	1·168	345	0·051	13·96	1·932	2·326	1·17	50
57. P	Colourless	1·033	110		3·04	2·753	3·315	1·13	34
				0·155					
59. P	Straw	1·156	335		12·29	3·421	4·119	4·24	103
60. P	Orange	1·210	451	0·208	16·65	2·995	3·606	10·66	301
61. P	Deep straw	1·142	272	0·125	10·87	2·271	2·734	7·18	263

[1] Relative conductivity $= \frac{1}{R} \times 10^4$.

Conductivity.—As shown by Graph A, and the figures in Table II, the relative conductivity of the samples varied to a remarkable degree. The figure recorded under the heading "relative" conductivity is deduced from $\left(\frac{1}{\text{actual resistance in ohms}}\right) \times 10^4$). The highest figure recorded was given by sample No. 7 (supplied by a trade plater) and the lowest was from sample No. 19 (another trade plater) which showed the remarkably low figure of 75.

The average conductivity is interesting as shown by the following comparisons :—

	Trade Platers.	Private Firms.
Average of several different vats	254, 287, 308, 333	362, 286, 200, 357
	277, 129, 254	228, 353, 326, 224
		332
Grand average	263	296
Minimum average of individual firm	129	200
Maximum average of individual firm	333	362

The conductivity is obviously influenced by the "free cyanide," silver, and carbonate contents. A comparison for example of samples 32 and 51 is instructive since the conductivity of these is practically alike, but they differ widely in composition as shown below :—

	Pot. Carbonate gr/100 c.c.	"Free" : Combined KCN per cent.	Silver oz./gall.
No. 32 . .	2·15	383	1·908
No. 51 . .	19·67	5	5·00

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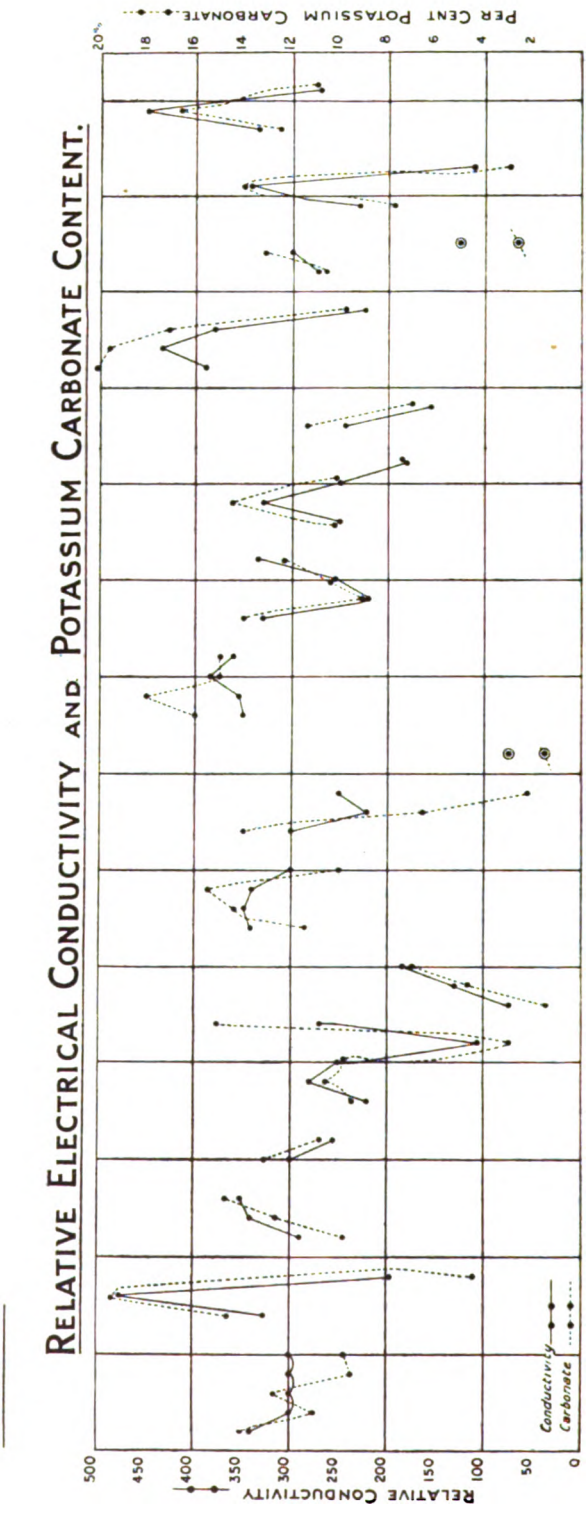
GRAPH A.



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With the exception of these two samples, *the conductivity appears to be largely a function of the Carbonate Content*, as is strikingly shown in Graph A in which the carbonate content and conductivity are correlated.

Carbonate Content.—This constituent, as will be seen from a reference to Table II, varies from 1·72 grams per 100 c.c., in sample 33 (solution only six months old) to 20·24 in sample 48, which is said to have been in daily use for thirty years.

It has often been suggested that the reason for the "kinder" or more satisfactory working of *old* silver plating solutions was due to the gradual accumulation of carbonate from the decomposition of the potassium cyanide. The results obtained by the Authors amply confirm the free conductivity of such heavily weighted carbonate baths, strikingly shown in Graph A. It is the Authors' intention to carry the investigation farther in this direction by the use of synthetic solutions of increasing carbonate content.

Note.—Potassium carbonate, as is well known, is used in large amounts in the manufacture of cyanide, and assuming that the ferrocyanide of two decades ago was much less pure than that at present available, there is little doubt that substantial percentages of carbonate entered the original solution from this source at the time of its preparation, altogether apart from that which resulted from decomposition in working the bath or the action of the air.

It is somewhat anomalous to have to suggest that the 70 to 80 per cent. cyanide of the early platers gave, by reason of such impurity as it carried, a *better* plating solution than one can get from the present purer salt containing upwards of 95 per cent. KCN.

Silver Content.—One is struck by the extraordinary wide limits found in the silver content of the solutions:—

The lowest contained	0·64 troy oz. per gallon
and the highest	5·00 „ „ „ „

Comparing the solutions used by "platers to the trade" and the private manufacturer we find that the former runs solutions of 0·5 to 1·5 oz. per gallon lower than the latter.

The following comparison of averages may be useful:—

	Trade Platers.	Private Manufacturers.
Average silver content in oz. per gallon . .	2·24 2·40 1·23 1·40 2·12 2·14	3·22, 2·05, 3·45, 2·07, 3·45, 1·73, 3·88, 2·30, 2·90
Grand average . .	1·92	2·70
Minimum „ . .	1·23	1·73
Maximum „ . .	2·40	3·88

Free Cyanide Content.—The majority of text-books prescribe for the preparation of a new silver-plating solution an amount of "free" cyanide equivalent to that required to precipitate the silver as AgCN. That is, the relation of the "free cyanide" to the combined cyanide (AgCN . KCN) should be as 1 : 2, *i.e.* 50 per cent.

It will be observed from Table II and Graph C that a very wide variation of this figure obtains in practice. Particularly does the maximum figure show an excessive use of cyanide almost amounting to *waste*—thus sample 60 shows 10·66 oz.-per gallon (practically a 7 per cent. solution of free cyanide) as against 0·29 in sample 51.

The theoretical proportion of 50 per cent. is far more often exceeded

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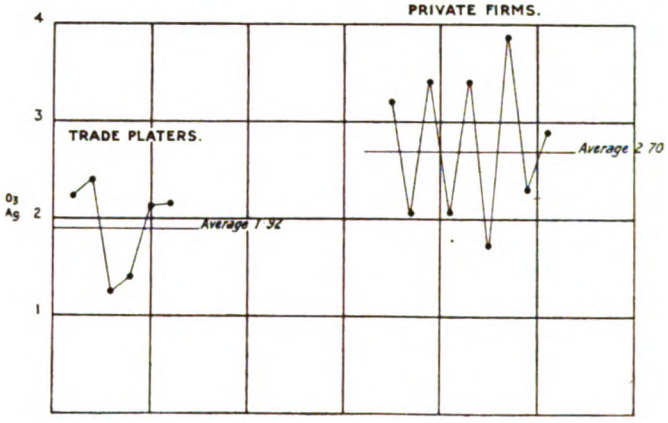
GRAPH B.

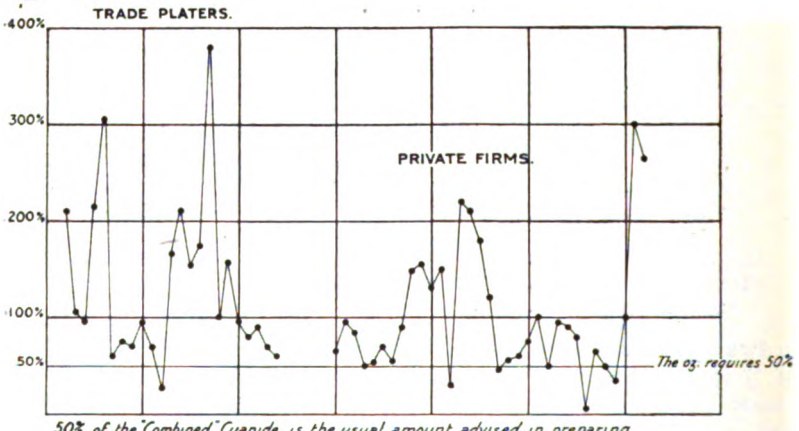
GRAND AVERAGE SILVER CONTENT.

Oz. troy per gallon.



GRAPH C.

PROPORTION OF "FREE" TO "COMBINED" CYANIDE.



50% of the "Combined" Cyanide is the usual amount advised in preparing the original bath.
In most cases it will be seen that this proportion has been greatly exceeded

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than otherwise, the variations being 5 per cent. as a minimum to 383 per cent. as a maximum; and, moreover, as there is very little difference in their conductivities, the use of an additional 378 per cent. KCN is uneconomical in view of the almost prohibitive price of cyanide during and since the war.

It would be possible, by examination of the results in detail, to draw many useful lessons, but we think that such are capable of being deduced by the average trained plater, and may, it is hoped, furnish the basis for further research. It was indeed hoped to have embodied in this paper the determination of thiocyanates, formates, etc., but lack of time must be pleaded in view of the large amount of work involved. The authors hope to add an addendum with such particulars at some future meeting.

In conclusion, the authors wish to acknowledge their indebtedness to the University of Sheffield for their permission to carry out the work, and to tender their thanks to Mr. Byron Carr, Mr. C. H. Hainsworth, and Miss Bradbury for material help in the completion of this interesting research.

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A NEW MAXIMUM CURRENT DENSITY IN COMMERCIAL SILVER-PLATING.

By Frank Mason, A.M.I.E.E.

During extensive researches on the physical structures of electro-silver deposits, which are at present being carried out at the University of Sheffield, the author observed that in certain instances exceedingly fine deposits of silver were obtained at an extraordinarily rapid rate.

In view of the enormous cost of plant for electroplating purposes, and the urgent need for increased output, the discovery was further investigated with surprising results.

It is well known that the maximum current densities used in the electro deposition of various metals from their respective solutions have been increased enormously by the introduction of moving electrodes. Cowper Coles' production of copper tubes is perhaps the classical example of this method, in which the current density was raised to over 200 amps. per square foot. Again, the deposition of nickel, tin, and zinc has been considerably accelerated by barrelling and similar processes.

None of these mechanical devices, however, are as yet available for production on a commercial scale of thick deposits of silver, such as are to be found on restaurant, hotel, and ships' outfits, and in fact all the best quality of electroplate.

It is also conceivable that flowing electrolytes would be conducive to higher current densities being used, in fact the author's experience of this, particularly in the laboratory, suggests great possibilities in this direction.

The disadvantages, further revealed as a result of experiments conducted on a commercial scale, altogether outweigh the benefits derived, from the resultant higher maximum current density. The difficulty of obtaining a fine reguline deposit of silver with a changing electrolyte, when treating large numbers of articles varying both in size and shape, is very great.

In criticising the quality of a deposit from the commercial standpoint, it is essential that it be judged with a view to subsequent processes to be operated on that deposit, and the final result obtained as the finished product.

It is admitted by all electroplate manufacturers that the deposits should be such that the characteristic mirror-like finish be obtained with least expenditure in labour after plating.

Microscopic examination of these silver structures enable one to make the following generalisation, that this ideal condition is to a large extent governed by the size and position of the crystals of the deposit. It is also clearly understood that other factors influence the labour involved in the process technically termed "finishing" but as these obtain, whatever the deposit may be, these factors will be ignored in this discussion.

It will be conceded that under normal and usual condition of commercial electroplating, *i.e.* an electrolyte composed of the double cyanide

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of silver and potassium with a percentage of free potassium cyanide, varying from approximately 40 per cent. to 70 per cent., the higher the current density used, the larger is the crystal obtained, until the crystalline structure is such that "finishing" is impossible, and the deposit is said to be "burnt".

This characteristic of ordinary silver-plating solutions has naturally set a maximum current density permissible which most authorities give as 3 to 4 amps. per square foot. Even at this rate the current density is considered in some cases to be too high, and results in what is technically termed a "hard" deposit.

In this connection the author may be pardoned in making some reference to a paper given before the members of the Sheffield Society of Applied Metallurgy in December, 1913, on "The Adhesion of Silver-deposits to High-grade Nickel Alloys," wherein the use of a small percentage of potassium carbonate was suggested in freshly-made silver-plating solutions as a means of improving the deposits. The excellent results obtained from old plating solutions naturally prompted this inclusion.

During the investigation referred to at the commencement of the paper, the electrolytes from which abnormal silver deposits were obtained always contained potassium carbonate. The metal from these was precipitated in a fine reguline condition, until the percentage of the latter compound reached the neighbourhood of 10 per cent., and the current conditions were normal. Any further increase produced large crystalline structures, very difficult to burnish or polish, and a current density of 6 amps. per square foot of cathode surface brought down a deposit from which the desired final "finish" could not satisfactorily be produced.

It was observed, however, that the solutions containing a higher percentage of potassium cyanide in conjunction with potassium carbonate, somewhat counteracted this undesired effect. On further investigation it was found that with a free cyanide content far in excess of that usually advised, and with potassium carbonate in very large quantities, not only could the current density be increased enormously, but that the deposit was of a finer texture altogether.

In order to present this matter in as useful and as practical a manner as possible, the author had the process installed on a commercial scale with most satisfactory results both as to rate of deposit and character of deposit. After depositing upwards of 8000 oz. of silver, an analysis of the electrolyte gave the following result:—

Silver	26·14	grammes	per litre.
Free KCN . . .	47·25	„	„ „
Potassium Carbonate .	165·00	„	„ „

The deposit from which the photomicrograph No. 1 was taken, was recently obtained from the foregoing bath, and under ordinary working conditions, but with a current density as high as 8 amps. per square foot of cathode surface, and was one of over 150 articles plated during the same period, and in the same bath. The deposit as illustrated in the micrograph No. 2 was obtained under commercial conditions as operated to-day, and not those forming the subject matter of this paper, and the current density of 3½ amps. per square foot used. The period of immersion in the depositing bath was the same in each case.

The difficulty of showing quite clearly the size, shape, and position of the crystals of a deposited metal by means of a photograph, is no small one. Thanks to the valuable assistance rendered by Dr. Thompson, the

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author is able to do this, and it will be noted that the micro-structure of No. 1 is almost identical with that exhibited in No. 2 micrograph.

The economy effected, when the maximum current density is increased over 100 per cent. as suggested in this paper, will be obvious to all. The

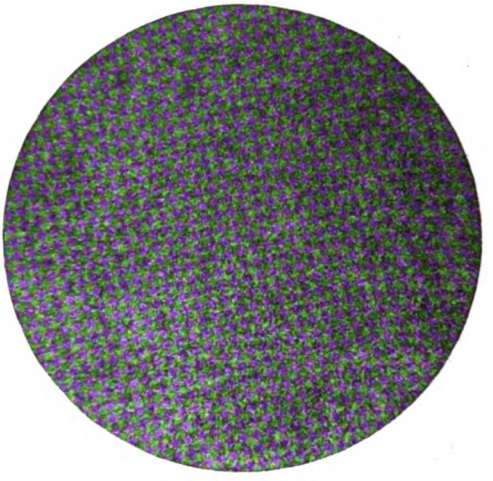

FIG. 1. (× 100 diams.)

reduction of time in deposition resulting in double the output, should be of considerable value, and the enormous saving in capital outlay in materials and plant, amounting in large establishments to many thousands

FIG. 2. (× 100 diams.)

of pounds, will doubtless be fully appreciated by the electroplate manufacturers of this country.

The author realises that this investigation is by no means complete, but is of the opinion that the publication of the results obtained at this early stage is fully justified because of the important bearing they have on the electroplate industry.

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The author acknowledges the enormous amount of work done on this and cognate subjects, in which investigators obtained good deposits of silver with a current density as high as 16 to 18 amps. per sq. foot experimentally. Commercially, the current density used is about 4 amps. per sq. foot. As the author is unaware of any publication dealing with *commercial* electro-silver-plating where deposits are produced as stated in the foregoing, it is claimed for this paper to be the first published process in commercial electro-silver-plating, wherein such a large current density is used, resulting in deposits of very fine crystalline structure.

In conclusion, the author begs to acknowledge his indebtedness, and to tender his sincere thanks to Dr. F. C. Thompson, for his valuable assistance in preparing the microphotographs.

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THE CRYSTALLINE STRUCTURE OF ELECTRO-DEPOSITED SILVER.

BEING AN INVESTIGATION INTO THE CAUSE OF CERTAIN RED MARKINGS ON FINISHED ELECTROPLATE.

By George Bernard Brook, F.I.C.

SOMETIME LECTURER IN NONFERROUS METALLURGY IN THE UNIVERSITY OF SHEFFIELD.

Some time ago the writer was called upon to investigate a trouble which was common to many silver-plating firms. It consisted in an appearance of a peculiar cloudy effect upon the burnished silver which was intensified by the usual subsequent rouge polishing, in which latter state it presented the appearance of reddish patches. These were particularly marked when held in a strong light and at a suitable angle. The common impression prevailed that such trouble only arose in summer and was by some attributed to the temperature of the electrolyte. As the cause was not associated with this suggestion it may be taken that the trouble was just as common in winter, but the poor light prevented the recognition of the fault.

It will be well to trace the processes through which the article passes whilst in the plater's hands. After receipt from the buffer or polisher, the article, made of german silver or britannia metal (and it is significant that such marking took place on both these basis alloys when plated, although they received slightly different treatment) is immersed in caustic alkali to remove the grease, in the case of german silver "quicked" (*i.e.* received a film of metallic mercury, which of course formed an alloy with the basis metal) and "struck" in the silver vat. It is usual then to "scratchbrush" the deposit and to replace it in the silver-plating solution until the desired thickness of silver is attained. The subsequent processes vary and may consist in scratchbrushing, or polishing with lime followed by rouge, or burnishing followed by hand polishing with rouge. A soap solution is used in the burnishing process.

Each one of these processes was investigated to locate the cause, as was the purity of the polishing materials employed or the character of the silver anodes used.

It was observed that the patches as a rule lay in one direction, and that generally in the direction of polishing and scratchbrushing. It was suggested that too drastic quicking or heavy scratchbrushing might account for the patchy appearance, but no satisfactory evidence was found to support this, as each of the conditions, one by one, was eliminated. The possibility of impurities in the rouge or the soap gave similar negative conclusions.

The electrical conditions were next investigated, particularly the phenomenon known as "power marks," and whilst it was found that the

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character of the deposit at such places was dense and dull, the ultimate burnishing resulted in a uniform polish after which the marks were barely visible. Moreover, they had the appearance of comparatively narrow streaks, and were mainly confined to the edges, generally having their source in some speck or sharp ornamentation of the metal.

The question then turned to the nature of the deposit as a whole.

FIG. A.

The possibility of such trouble arising from one vat, out of condition, was negatived by experiment, as it was given more or less by each and every compartment of some seven vats. Chemical examination was obviously out of the question, and so resort was had to a general microscopic examination of the deposited silver both before and after burnishing.

It was found that articles plated in the University, and which did not

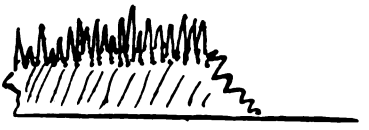

FIG. B.

show the peculiar marking after burnishing, had a surface that was relatively coarse grained, but the general level presented an undulating surface. It would have been difficult to obtain, in the limited time available, any micrographs which would stand reproduction, partly owing to the lack of contrast from the intense reflection from the white silver surface, and partly from the fact that it was difficult to obtain a microscopic flat field

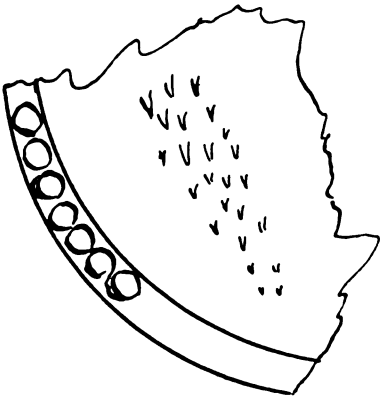

FIG. C.

in view of the articles being buffed by machinery. The accompanying sketches may therefore suffice to give an idea of the appearance of a section at 100 magnifications.

(*a*) Satisfactory deposit before burnishing (Fig. A).

(*b*) Unsatisfactory deposit before burnishing (Fig. B).

(*c*) Surface appearance of (*b*) after burnishing, showing patches under 100 magnifications (Fig. C).

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It was quite reasonable to think that the effect might have been caused by the size of the crystal, but the investigation showed that it was the *character* rather than the size of the crystals that led to the subsequent trouble. Thus if one burnishes a surface, whether relatively coarse or fine like that of (*a*), the final surface is substantially level and burnishes down uniformly, and hence shows no irregularity or patchiness either before or after rouge polishing. Whereas either machine polishing or burnishing of a surface like (*b*) would inevitably result in some of the needle-shaped crystals being merely laid down on the surface, the closeness

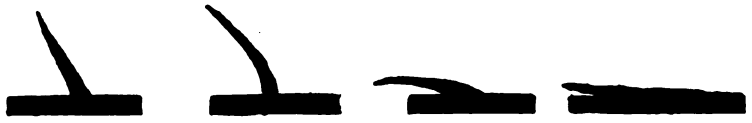

FIG. D.

with which such lie on the surface beneath depending upon the pressure imposed, and possibly the size of the crystals.

One can then readily imagine the bending over of an individual crystal under the action of the tool in steps as shown in section in Fig. D, and the surface appearance finally represented in Fig. E, where (*a*) is a crystal nearly laid down, and (*b*) points of crystals that are visible after heavy treatment.

It will be seen that the actual appearance of the patches as shown in Fig. C. is in agreement with the theory developed in Figs. D. and E.

Substantial confirmation was obtained on examining the edge of the

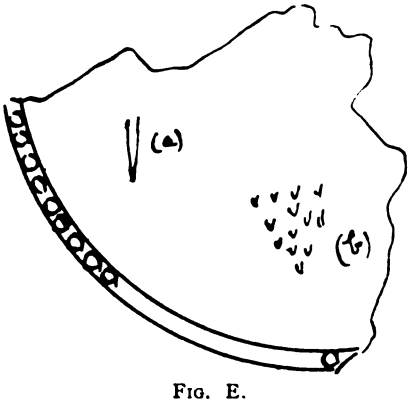

FIG. E.

defective dishes, which showed in an even more marked degree acicular crystals as shown in Fig. F. This needle-shaped crystal was always found where a high current density was used, and the author can only conclude that the speeding up of electro-silver deposition called for by the rush of work immediately following the war has tempted the manufacturers to overstep the limit of safety in the rate of plating. The "reguline" deposit has given place to an acicular one, and such needle-shaped crystals as are not laid down by the burnish retain in their interstices particles of the polishing powder, which collectively are visible to the eye as red patches.

It was maintained that the peculiar appearance was never found on spoons and forks, which in view of the great demand have been necessarily

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turned out at the highest possible speed. This is obviously accounted for by the fact that such articles present very little flat surface, and as explained it is only at a certain angle that the defect is obvious, so that the varying shapes and short radius curves of the fork or spoon help to hide it. On trays, etc., presenting plain flat surfaces it is comparatively easy to detect,

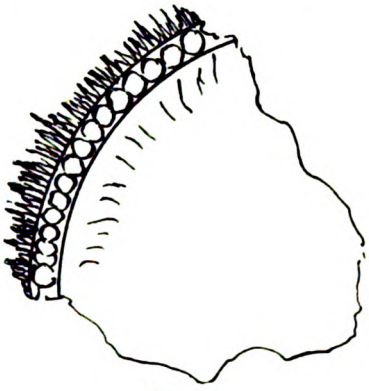

FIG. F.

and it is, moreover, on such articles that absolute freedom from this patch defect is called for.

The growth of individual crystals on the back of electrotypes serves to confirm the author's deductions. As is well known the rate at which the metal is deposited, after the mould is completely covered, is pushed to the maximum, and individual crystals of copper often develop which are fully 2 mm. in length.

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GENERAL DISCUSSION.

The **Chairman:** I feel sure you will all agree that we have listened to a very interesting series of papers. We may describe Mr. Barclay's paper as a very valuable contribution to the development of electroplating from the technical side. You will remember we had a very interesting paper from Mr. R. Leader, before the Institute of Metals in 1919, dealing with the historical side of electroplating, and Mr. Barclay has gathered up the history from the scientific and technical standpoint. With regard to the other papers, it is to be regretted that the authors have not made any reference to previous work. The various references given by Mr. Barclay in his paper show that something has already been done in the direction in which Messrs. Brook and Holmes, and Mr. Mason have been working. Their work is, however, of interest and value since it has confirmed that of previous workers, and also added some new data. The meeting will now be thrown open for discussion, and it is hoped that members will not hesitate to join in the discussion and condense their remarks so that time may not be lost. I will ask Dr. Thompson to open the discussion, as he has received two written contributions to the discussion on the papers dealt with this evening.

Dr. F. C. Thompson: The first communication I have to read, which is of some theoretical interest in connection with electrodeposition, is from Mr. Sidney Skinner, of the South-Western Polytechnic Institute, London. It is a paper read before the British Association at Glasgow in 1901, and I think the essence of the Paper, which is entitled "A NOTE ON A COMPARISON OF THE SILVER DEPOSITED IN VOLTAMETERS CONTAINING DIFFERENT SOLVENTS," is conveyed in the following quotations :—

"In 1892 Schuster and Crossley showed that when the same current is passed through two silver voltameters containing silver nitrate in aqueous solution, one voltameter in a vacuum and the other in air, about 0·1 per cent. more silver was deposited in the vacuum than in air."

That is perhaps of some interest, in connection with the reference Mr. Barclay has already made to the influence of air or hydrogen on the character of the deposit.

"Werner found that a silver nitrate solution in pyridine gives by the rise in the boiling-point of the solvent a nearly normal molecular weight for the salt; and Kahlenberg found that the solution was an electrolyte, and could be used in the silver voltameter: but that, contrary to what follows, more silver was deposited from aqueous solution than from pyridene solution by the same current" —indicating that in pyridene the silver is not appreciably ionised as it is in water.

"The deposit from the pyridine solution is continuous, and forms a hard coating: it is washed with water in which both pyridene and silver nitrate are soluble."

By "continuous" the author apparently intends to draw a distinction between

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that deposit and what he calls the crystalline deposit obtained from the aqueous solution.

"The first result of these experiments is clearly that all the deposits from the pyridine solutions weigh more than those from the aqueous solutions. . . . So that for these values of current the deposit from pyridine would weigh almost the same as Schuster and Crossley found for a vacuum, which, it will be remembered, was ·1 per cent. higher than in air. . . . The aqueous voltameter seemed to work best with the large currents, ·5 to 1 ampere when the crystals were small, hard, and closely packed. At the lower values of current the silver crystals were thin, long, and friable. At the lowest value they were again small and hard."

The author's conclusions are :—

"(1) That Faraday's law holds to within ·24 per cent. in the mean for silver nitrate when dissolved in two different solvents ; (2) that for current values of ·07 and ·5 to 1 ampere in the given bowls the amount of silver deposited from a pyridine solution of silver nitrate is nearly the same as that deposited from an aqueous solution in a vacuum ; and finally, that for current values between ·1 and ·5 ampere more silver is obtained in the pyridine voltameter than in the aqueous voltameter."

Perhaps the most important application of that is to be found in the remarks of Mr. Barclay, who emphasised the importance of the organic material present in the bath, and in the paper presented by Mr. Hughes on the influence of colloids. He showed, too, that comparatively small quantities of some of these colloidal or organic impurities exercise a very important influence on the character of the deposit obtained.

The second communication comes from **Mr. W. E. Hughes** himself, on Mr. G. B. Brook's Paper, "THE CRYSTALLINE STRUCTURE OF ELECTRODEPOSITED SILVER". You remember that the essential feature of that paper was that Mr. Brook considered that the red marks obtained on the polished surface were due to the crystals being flattened over, and holding rouge in position in that way. Mr. Hughes says : "I am particularly interested in Mr. Brook's paper, because, shortly before the war, I had an experience very similar indeed to that which he describes. After some investigation of the matter I was, unfortunately, compelled to leave it in other hands. A careful reading of Mr. Brook's paper leaves me by no means convinced that he has solved the problem he had to face. Such work as I was able to do in the case that confronted me caused me to suspect sulphide. There were traces of sulphur in the deposit itself, and my assistant found it in both the potash and the plating solution. The cause of the trouble was certainly not—in my case—excessive current density, since (1) tests on some solution from one of the tanks on a two-gallon scale in the laboratory gave similar results to those obtained in the workshop, and (2) when a vat was emptied, cleaned out, and a new solution made up in it, the new solution, when worked under the same current conditions as before and on the same classes of articles, gave deposits that showed no blemish. My experience differed from that of Mr. Brook in that the dark area could be seen on articles having surfaces of varying curvature, such as sauce-boats, sugar-basins, and spoons, as well as on flat ware. But, like Mr. Brook, the discoloration (if it can be called such) was visible only in a bright light and when the light was reflected from the surface at a certain angle—in my case, somewhere about 45°. It may be that the defect of which Mr. Brook tells us in his paper was not the same as that which I had to deal with : it is difficult to say without seeing, side by side, illustrative articles. Our differing conclusions may be due

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to this fact. In any case, Mr. Brook is to be congratulated on two matters; namely, (1) on bringing this particular "trouble" before a meeting where it can be discussed, and (2) on the method he has adopted to solve his problem. The microscope has, up to now, found too little use in dealing with difficulties met with in the plating shop. In my experience, the examination of deposits with the microscope often affords useful assistance, and should be resorted to much more frequently than is at present the case."

I have only one other thing (added Dr. Thompson) that I should like to say, and that is, that in some respects the present meeting is undoubtedly a historical one. In America and on the Continent, a great deal more attention appears to have been paid to the problem than has been the case in this country, and the Faraday Society, in bringing together the large number of papers which have been presented at this meeting, has done something which has never before been attempted, to my knowledge, in this country.

Mr. A. Bowker: It is a source of great satisfaction to me to be at such a representative meeting of those who are engaged in the practical process of electrodeposition, and also of those who take a purely scientific and theoretical interest therein. This is exactly as it should be. It augurs well for the future of the industry when both these sides are interested together, because one is the natural fulfilment and assistance of the other. Although essentially a worker, I have always realised the importance of scientific investigation in connection with the industry, which is evidenced by the fact that, after earning my living for thirty years at electroplating, I came to this institution and took a course in electrodeposition from a gentleman well known to many of you here to-night, Mr. W. R. Barclay.

There have been many points of great interest raised to-night, but I would confine myself strictly to the consideration of one question, and that is the question of high current density. We must guard against working out a logical deduction until it becomes a physical absurdity. A proposal, as well as being scientific, must be practical. I don't say that a current density of eight amperes is impossible to be worked. But it is the deduction that I quarrel with. In the paper referred to the author says: "The economy effected, when the maximum current density is increased over 100 per cent. as suggested in this paper, will be obvious to all. The reduction of time in deposition resulting in double the output. . . ." Now I confidently maintain that no plater in this town, by the simple method of increasing the current density by 100 per cent., would double his output. Current density is only one factor among many others. What about the preparation of the articles? This implies that all those at the present time engaged in a plating shop are only doing half what they could do if they could get it out of the vats quicker. I submit that is absurd, and I think most of the people here will support that view. Then the author goes on to say: "The enormous saving in capital outlay in materials and plant, amounting in large establishments to many thousands of pounds, will doubtless be fully appreciated by the electroplate manufacturers of this country". I confidently affirm that the large establishments won't save a penny, and for one or two reasons which I will give; objections from the practical point of view. In the first place, this heavy deposition at high speed is contrary to the law of nature. Slow growth always goes with durability. Why should articles which are going to be in constant wear for twenty years be rushed for a few minutes at the plater's?

Other objections from the practical point of view are these: Firstly, the objection of preparation. If the output is going to be doubled by the adoption

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of increased current density, the means of preparation will have to be doubled, which will mean a double staff. It must be, unless the men at the present time are only doing half of what they are able to do, and I think no one will admit that. Another question is the question of overweight. Every plater knows what that means if these things are being worked at double the speed, and for any reason whatever the plater leaves them in a few minutes too long, when he uses a high current density the amount of overweight will be doubled. Another objection is the unequal deposit which always takes place between those articles at the end of a rod and those in the centre, and I think it will not be at all out of the way to affirm that there would be at least a difference of 10 per cent. in the deposit between a dozen spoons and forks at the end of a rod and a dozen on the same rod in the centre. This would be absolutely fatal to guaranteed deposits. I maintain, and I think I can prove it practically, that any plater will do more work with two vats working at four amperes to the square foot than he would do with one vat working at eight amperes. Finally, there is one question that I should like to ask the author of this paper. We all know that he is in complete charge of one of the largest and best equipped plating establishments in the kingdom, and that he is with a firm whose reputation is deservedly world-wide. Has this method been adopted universally in his own shop, and if not why not?

Mr. W. R. Barclay: I am very sorry indeed that I have not had an hour with the authors of both these papers before this meeting. I desire to be very appreciative, because no one but those who have actually done scientific work in connection with the electrodeposition of metals knows exactly how much work is involved in such papers as these, and I want my first word to be a very real appreciation of Mr. Brook, Mr. Holmes, and Mr. Mason. Now I wish to suggest to both authors that they would be very well advised if they would very carefully study previous work on this subject. The Chairman has already mentioned that, and I also think it is a regrettable feature of these papers that neither of them, apparently, have taken the trouble to investigate thoroughly the work of previous workers. Now a careful study of Brunner's work, as an example, will reveal that a current density of eight amperes per square foot is by no means the maximum that can be reached. Admittedly, of course, his results were laboratory results, but his tables show very conclusively that, fine, smooth, easily polished deposits—as he calls them, lustrous—were obtained with current densities not of eight but up to twelve and fourteen amperes per square foot in the laboratory, without any potassium carbonate at all. In my own work in this University years ago, and in the book I published with Mr. Hainsworth in 1912,[1] I not only referred to the influence of potassium carbonate in old solutions, but I pointed out that potassium carbonate could, with perfect safety, be used in preparing a new solution; in fact I described that as a very simple way of making a silver solution without the risk of chemical waste. But the influence of potassium carbonate is very closely allied to the influence of free cyanide, and, coming to Mr. Brook's and Mr. Holmes' paper particularly, I venture to submit to them that they would find very much food for thought if they would study the very valuable figures they themselves have furnished with regard to specific gravity. They would then find that their highest conductivity usually follows their highest specific gravity without necessarily following the line of potassium carbonate content. Admittedly, potassium carbonate plays a very great part, but it is by no means the only salt present, and the researches not

[1] "Electroplating," Barclay and Hainsworth, Arnold, 1912, pp. 191-194.

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only of Brunner but of Frary and Porter, to which I have earlier referred, have shown very clearly that all these potassium salts have very much the same conductivity as free potassium cyanide—that is to say that potassium cyanide, potassium chloride, and potassium carbonate, all of them add to the conductivity of the bath ; and I venture to submit that no results in the way of high current densities can possibly be successful unless, along with the presence of potassium carbonate or potassium chloride, or anything else, you have a balanced supply of free potassium cyanide. Mr. Mason's paper itself reveals that he had present a very considerable excess of free cyanide as well as potassium carbonate, and the figures furnished by Mr. Brook and Mr. Holmes confirm very thoroughly, in my opinion, that point.

To sum up, the points brought out are : firstly, that potassium carbonate and other salts do add to the conductivity of the solution (that is admitted : it is proved by Mr. Brook and Mr. Holmes' paper, but it was proved earlier by Frary and Porter) ; secondly, that a higher conductivity will allow you to use a higher current density. But I do wish to emphasise, for the benefit of practical platers here, the absolute necessity of co-ordinating the three factors of potassium cyanide, silver, and current density. Then you can have potassium carbonate present with absolute safety, and indeed with advantage, up to a certain point. Personally, I would prefer very much to start with a low quantity of potassium carbonate, knowing perfectly well that if I have a high free cyanide content I shall very quickly convert part of that into potassium carbonate.

Mr. Nicol : I want to confine what I have to say to Mr. Mason's paper. We looked forward to it with a very great amount of interest. With regard to the electrical side of the question I am of the opinion that Mr. Mason is on the right lines when he suggests that potassium carbonate exists in the solution. Observation of solutions containing a large proportion of potassium carbonate seems to prove that in a remarkable degree. To come down to the practical side of the question I want to support Mr. Bowker in all he says about the matter. With regard to the question of double current density meaning double output let us take a practical illustration ; to make it clear to a large proportion of practical platers that I see here. If you take a piece of plate 24 inches in length and 18 inches deep you have a surface of 5 square feet. To work that at the current density that Mr. Mason has indicated would mean working at the rate of 26 ounces per hour. To put that as a serious proposition is a very big thing indeed. Then there is the question of the distribution of the deposit. Some of us here have remarkable evidence upon this question. In a lecture some time ago we saw some copper plates upon aeroplanes and the lecturer threw on the screen some remarkable photographs. We saw that the copper deposits had distributed themselves over the side of the engine, and came out on the side cylinder. With regard to the silver-plating business we have to consider a simple instance. Are we going to get the same proportion of deposit out under the new conditions as we do under the present conditions? These are matters which are vital because you may have too high an amount of silver in the deposit or too high a proportion of density. It is a distinct difficulty. I should like to express my appreciation of Mr. Mason's paper and say with how much interest we have all followed every word of it.

Mr. Jefferson : It is almost a pity that we have so many papers of the same class in one evening because each one brings out things which it would be an advantage to discuss for a considerable time. I think I am right when I say

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that Mr. Barclay in his paper touched the crux of the whole question which is agitating the minds of those who are engaged in the electrodeposition of silver, when he says the question of organic impurities is a most vital matter in these electrolytes. Now I believe that would have been demonstrated more clearly if he had referred to the addition of colloids to the solution. I do not know whether it is the practice in the electroplating shops of to-day, but I know that it has been the frequent practice of late to add sulphide of carbon to the ordinary plating solution in order to accelerate the deposits and bring about a more even deposit. I suggest that the most serious impurities which have been found in the solutions have been sulphur and sulphides. If these impurities were left in, then a good deal of trouble was bound to result.

I do not agree with Mr. Mason when he suggests that it is practicable to plate with a high current density. It is possible, I know it has been done, and I think a good deal of credit is due to Mr. Mason for bringing the matter before us.

I should like to say just a word regarding the structure of the deposit which produces the red colour referred to by Mr. Brook. Has he considered the possibility of the metal not being properly prepared before it goes into the electrolyte to receive the deposit of silver? In my opinion that is most important; if you want a smooth deposit you must have a perfectly smooth surface to begin with. I suggest that a good deal of the trouble that has existed in this direction is not so much a question of crystalline structure or of density, but is largely a question of mechanical labour and methods of working. To-day it is not easy to go into any finishing shop and find the old methods of liming plate work. I have seen an article coming from a vat very badly discoloured and I have seen another article from the same vat which had been carefully handled by the finisher which did not show a trace of burning or of red deposit.

Mr. Byron Carr: I would refer to a paper which I read some time ago, the writer of which was called upon to investigate a trouble which was common to many silver-plate firms, and which consisted in the peculiar patchy red appearance that has been referred to. I was sent for to give my opinion as to the reason of the production of the red colour, and I was told that it always occurred more in warm weather. I thought that the weather would have a considerable influence on the conductivity of the solution, and consequently the deposit might be a little coarser. I held that opinion for a very considerable time, in fact until after Mr. Brook had written this paper, and I proved distinctly that it was the rouge that produced the red patchy coloration. It probably is due to the burning effect which has been mentioned, and I dare say Dr. Thompson can remember something similar occurring when rouge was used for polishing steel specimens. If the rouge dried on the polishing buff, it stuck to the steel and it could not be removed very easily; it had to be polished off again. I thought that a similar action might take place in brushing, and to elucidate that a considerable number of experiments were performed by treating plating solutions in a most brutal manner, both as regards temperature and density of current, but I utterly failed to produce any of those remarkable acicular crystals which have been depicted. Now I should be greatly obliged if any plater who can produce these crystals will send me a sample of them. Since this paper was written I have been down to a place where they showed me some patchy work which was bad indeed. I said I thought it must be due to the rouge and to the polishing, and I suggested that if these crystals were broken down by the burnish, and the surface removed and made perfectly smooth to the eye, and then hand-polished

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they would see no rouge marks. Well, a tray was plated, and it was burnished. It was then handed over directly to be rouged and when done it was beautifully marked with the rouge, so evidently that was not due to the polishing effect of the dollies. Then I was sent for again, this time not to inspect an electroplated article but a silver one, and that silver one was as beautifully patched as any electroplated article you ever saw. Now, while that had not not been plated, it had been dollied, so I think that should dispose of the theory of acicular crystals being burnished down and then forming cavities for the rouge. Again, some work is polished before it goes into the plating vat in cases where it is desired to keep a polished surface on the article when it comes out of the vat. Here very little silver is put on, and the thickness of the deposit cannot be enough for the function of any acicular crystals. Nevertheless these articles develop the redness quite as much as the electroplated ones. I think you will see that the trouble is not due entirely to the electroplated surface. Some small experiments were performed on silver surfaces—the ordinary standard silver. The surfaces were hammered, buffed and polished, and then burnished and placed under the microscope. Now you could see from the surface marks that the silver had really been torn, but I doubt as to whether that torn surface would hold the rouge and produce the red patches. Anyhow I have endeavoured to show you it is not entirely due to the plating. There is one other point I should like to mention. I was speaking to a plater in this town only last week, and he said that he plated trays for two different firms. The trays of the one firm always developed this red colour, while those of the other did not, and the only reason he had for that was that the trays of one firm were finished by one man and the trays of the other by a different man.

Mr. Price: I should like to say, in as condensed a form as possible, that I do not agree with the views Mr. Mason has put forward to-night. I think his proposal is outside the possibilities of practicability. There is one little thing I would like Mr. Mason to have shown to us on the screen ; namely, micrographs of the surface previous to electrodeposition to compare with the surface after deposition. With reference to the remarks of Mr. Bowker, there is no doubt still in the mind of the Sheffield electroplater a fear of trying to go forward ; and I am going to challenge my friend Mr. Bowker with being tainted with that fear. I think that if many electroplaters would interest themselves in experimental work based on scientific propositions put forward, something would be gained, and not least a little more confidence in ourselves, especially in the case of the deposition of silver.

I have been much interested in the deposition of silver under high tension for the last six months, in connection with a plant I am installing for the rather rapid deposition of silver on deep-draughted reflectors for motor lamps. I have been astonished at the results. I have taken an ordinary reflector, 8 inches by 5¾ in depth and introduced a small anode of silver wrapped only with a sing'e cover. I found then that the pressure necessary to give a rapid deposit had to be increased. I increased the rate fourfold to sixfold, and found that the deposit of silver was still remarkably beautiful and superfine. I have been so bold now as to try putting a rather thick covering of felt on the anode, and bringing it closer to the cathode and still I get very good results. So I say try using a high E.M.F.—you may get some valuable results and experience, as I have in this case, and in depositing other metals. Do not think that what you have been dolng for twenty years cannot be improved on.

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I should like to make a remark upon the matter of atmospheric conditions and temperature. I was in a plating department in Sydney, N.S.W., where it was a little warm—sometimes 112 in the shade—and I was surprised at the difficulties in carrying out operations uniformly throughout the whole of a week's silver-plating. Moreover, the atmosphere of Sydney is heavily salt-laden, and that led to trouble in the plating department that I had never experienced before. It is worth bearing in mind the possibility that temperature and atmospheric conditions are circumstances that may trouble the plater.

Mr. Lobley: As one new both to the practical side of plating and to Sheffield, may I be permitted to ask a few questions and make a few remarks. In the first place, Mr. Brook's paper on the crystalline structure causing the red patches appears singularly unconvincing, and Mr. Carr seems to have given the deathblow to the theory. I should like to ask whether the manufacturers who experienced this trouble accepted Mr. Brook's explanation; whether, in fact, they had been speeding up and increased their current density, and whether, if so, they got rid of their trouble by reducing the current density. We have not been told that at all in the paper, and I think the whole thing is pivoted round it. Secondly, with reference to Mr. Mason's paper on increased current density, I am quite in agreement with Mr. Bowker that, obviously, doubling the current density does not mean doubling the output, yet, when Mr. Bowker says that it is against the laws of nature to attempt to increase it, I cannot agree, because at what point are we going to draw the line between slow and fast deposition? His point that going slowly is always better, we know, cannot be carried to a logical conclusion—a very slow deposition is not good. But there is one suggestion which may be useful. If Mr. Mason furnishes us with a plating solution which is capable of being used at a higher speed, is it not possible that such a solution, used at the normal speed will give better results as regards the equal deposition of the metal on the different parts of the object? Mr. Bowker has told us about the 10 per cent. greater deposition that is possible at the parts nearer to the anodes. By increasing the conductivity of the solution I should imagine that we should get a more even deposit. It would be interesting to know if I am correct.

Capt. S. W. Turner (*communicated*): I cannot agree that the trouble investigated by Mr. G. B. Brook is as common in winter as in summer. Whilst poor light may assist the passing of the fault yet the loss and worry caused by such oversight are such that this blemish is very carefully sought for, notwithstanding which it is very rarely discovered in winter.

The seat of the trouble may be: 1. The article before it is plated; 2. The deposit; 3. The subsequent treatment.

Considering the first of these possibilities:—

In the case of light deposits it is conceivable that irregularities in the basis metal may be apparent through a thin coating of silver; but with heavy deposits such as those to which the writer is accustomed this is not likely to be the case.

Turning to the third possibility:—

On very rare occasions the writer has observed this discoloration on small articles such as sauce-boats and teapots, sometimes on entrée dishes, but usually on salvers and trays, that is on large plane surfaces. All these large articles receive the same mechanical treatment by the same individuals using the same

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polishing materials and are subsequently hand-treated by different persons who all use the same materials.

They are paid for by the piece after being passed by the head polisher and if rejected they have to be refinished without extra charge. Consequently both the chief finisher and the burnisher are on the look out for the first sign of red.

Nevertheless it often happens that an article reaches the final stage before the blemish is discovered. The writer remembers one particular 24-inch tray: When laid on a flat surface in strong sunlight it appeared excellent. The eye could be moved to any position and no defect was apparent. But if the tray was held vertical a rusty streak was at once noticeable. It had to be refinished and polished five times before it was satisfactory. On each occasion the mechanical treatment was the same and the same materials were employed by the same work-people.

It was always necessary to hold the tray vertical to observe the discoloration. The only change was that by repeated finishing some of the deposited silver had been removed and the inference was that the trouble lay in the deposited silver.

Similar instances have been noted but not so bad as the one cited. The trouble has almost always occurred in hot weather and amongst a batch of articles which have been plated at the same time.

The observations of the writer lead him to think that the seat of trouble is the process of deposition or possibly the period of waiting after the article has left the vat and before it is finished. The colour of the stain has been noted to vary from a chocolate brown to a rouge red. Like Mr. Byron Carr the writer has known it to appear on silver, though once only, on an 18-inch salver which had never been electroplated.

Mr. Frank Mason replying to the discussion said: When I came into the room to-night I was somewhat taken aback at the remark of a gentleman who said: "I congratulate you on your paper but you are rather too reticent about it. What you are going to say I have known for years." In reply to Mr. Bowker I may say that I thoroughly realise that in regard to doubling the output that there are other factors besides current density in the deposition of silver. The question of labour, as I think I mentioned in the paper, was quite outside the discussion. I knew very well that the audience to-night would know sufficient about electroplating to make it unnecessary for me to mention that because you are putting a double current on a given area it would eliminate preparation. I believe that the current density throughout this city is 3½ amperes per square foot, and if you use 8 amperes square foot it means of necessity, provided the labour is there, which one takes for granted, that the output from that particular plant would be doubled. Where large quantities of plating are done, such as happens at one or two plants in this country, it would mean actually a saving of thousands of pounds. The cost of one vat of silver alone with everything included was, at the time I introduced this, about £300 and you have not got to get many vats at £300 to get up to a thousand. I hope that I have made it clear to everybody that I certainly did not intend to put before any audience that the increase of current density by 100 per cent. would do away with the necessity for preparation of the work.

From my own experience in the laboratory I am inclined to agree with Mr. Lobley in what he says about current density and even deposits. When Mr. Bowker spoke of deposits uneven to the extent of 10 per cent. I think he was referring particularly to spoons and forks, where you may have a couple of

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spoons or forks at one end of the rod or vat which will be higher or lower than those at the other end, or in the centre. On some future occasion if I have the opportunity I should like to give a paper illustrating the electrical formates of the electroplate plant. I believe in most cases the alteration is brought about not by the alteration of the current density but by the alteration of the formates which reduces the figure to 2 per cent. The question of the alteration of the current density does not in any way interfere with that.

There is another point which I should like to mention here, and that is the question asked by Mr. Bowker as to whether I have made use of the new current density in one of the largest electroplate establishments in this city which I have the privilege of controlling. My answer is that a plant has been running for six months under those conditions, which have doubled the output of that particular plant.

Mr. G. B. Brook (*communicated reply*): It was unfortunate that the papers were grouped together and not discussed individually, as it is somewhat difficult to say at times to what paper the speakers are referring.

In reply to the conjoint paper by Mr. Holmes and Mr. Brook, the authors would say that so far as he is reported, Mr. Barclay seemed to have confused their paper with that of Mr. Mason. They had no knowledge of Mr. Mason's paper before the meeting. The authors would say that they were aware of the published data quoted by Mr. Barclay, but they did not think it bore specifically on the subject of the paper; the paper was not intended to be a thesis on the relative conductivities of solutions of metallic salts, but to set out, as its title of "The *Chemical Composition* of Old Plating Solutions" conveys, data on many such solutions, which had hitherto been confined to the publication of one or two odd analyses. Here was an extensive summary (as the preface indicated), of practically the whole of the solutions used in the Sheffield plating trades, and as such has an obvious permanent value. Mr. Barclay points out that the specific gravity is a measure of the conductivity—this might be expected, but does not indicate to what constituent the conductivity was mainly due. On the question of potassium carbonate we should hardly like to accuse Mr. Barclay of inconsistency, yet we think that, since the K_2CO_3 content plotted against conductivity gave a straight line (despite the fact that KCN and Ag content were varying within the widest limits), our only conclusion that "the conductivity appears to be largely a function of the K_2CO_3 content" was at least a very modest one.

Unfortunately we had not access at the time to Barclay and Hainsworth's "Electro-plating," as our copy had been "borrowed and not returned," so we must apologise to the authors for not quoting the reference they give. We have since had an opportunity of consulting the work, and regret to find no reference to the important subject of potassium carbonate in the index. On page 192 the authors recommend the preparation of a plating bath by solution of silver carbonate in potassium cyanide, evidently under the implied and stated opinion that the carbonate is "not objectionable". Such method of preparation, it may be observed, would only result in a content of 1 to 2 gms. potassium carbonate per 100 c.c. Later reference is made to a 30 year old solution containing 13 gms. per 100 c.c. K_2CO_3 which is said to give "completely satisfactory results". From which one would think the authors were agreed with us on the advantages of potassium carbonate as a desirable constituent. On the same page, however, one finds it stated that "the accumulation of potassium carbonate makes the solution *sluggish*" and recommends its removal by precipitation with barium cyanide!

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The authors of the present paper, having examined a large number of such 30 to 40 year old solutions, reported on as giving the best results in plating practice, found that they contained upwards of 20 gms. per 100 c.c. potassium carbonate. Moreover, the only essential difference between these old (and highly valued) solutions and those freshly prepared, was to be found in the carbonate content.

In reply to the discussion on the paper on "The Structure of Electro-deposited Silver," the author much appreciates Mr. Hughes' remarks, and agrees that the trouble investigated by Mr. Hughes was probably not identical with that met with by the author. In reply to Mr. Jefferson, he would say that there was no question of faulty initial preparation of the goods, nor was it traceable to the finishing—as the author pointed out, the defect was present, though not so obvious, in the burnished condition. Any subsequent "rouging," whether done by hand or machine, gave as a *secondary* result the red tint referred to. Had the polishing material been green, the final tint would also have been green. In part, the author thinks Mr. Jefferson, and possibly also Mr. Carr, is confusing this phenomena with the "fire-marks" in silver.

Mr. Carr states that the rouge *produces* the red patchy colour—the author would refer him to the previous paragraph. The same contributor first of all denies the existence of such acicular crystals, and a few lines later says that he himself "had these crystals broken down by the burnish," and subsequently the surface was buffed smooth "to the eye". There lies the whole point—would the surface so smooth "to the eye" be described as such under 100 magnifications? For it must be remembered that the acicular crystals are microscopical in size.

Most of the speakers mix up the observed fact and the theory advanced to explain the phenomena. There is no doubt of the existence of acicular crystals—they were seen by Dr. Thompson, Mr. Mason, and others—indeed, the writer thought it superfluous almost to state the fact, as most platers have seen massive individual crystals of copper and other metals growing from the face of the deposit. The theory advanced, *viz.*, too high current density, is, of course, a matter on which opinions may be divided. But in reply to Mr. Lobley (whose "death blow" was only a *stage* one), the author cannot think he can have read the paper carefully, as it was clearly stated that such acicular crystals were not given at low current densities; further, in reply to the same speaker, the author learned that he speed of deposition, at the time of the trouble, was double what it was in pre-war days.

[At this point the author would like to say that these remarks relative to crystal size and C.D. refer to *normal* solutions, and not to such solution as is dealt with in Mr. Mason's paper. As he has not seen this paper, he can only gather from the proof of the discussion that Mr. Mason used a bath of special composition for high C.D.]

Mr. S. Ward Turner's remarks confirm the writer's deductions, and Mr. Carr will note that not before *repeated repolishings* of the surface of the red patchy sample, referred to by Mr. Turner, was it possible to obtain a perfect clear surface. In other words, not until the over-laid acicular crystals had been removed by continued repeated buffing, was it possible to get a *plane* surface free from interstices in which the rouge could become embedded. Mr. Turner agrees that "the seat of the trouble is the process of deposition". Both he and Mr. Carr state that the fault is commoner in hot weather than in cold. If they will say it is more obvious in "summer" than in winter the author will agree, since it requires a good light to detect the fault, and then only when the article is held at a particular angle.

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The **Chairman:** We have had an extremely interesting and valuable meeting. The large attendances at the symposium have fully justified the expectations of those who promoted the meetings that they would be productive of good results.

I venture to express the hope this will not be the last of such meetings to be held in Sheffield. In summing up the papers that have been given to-night I think they have emphasised the importance of organic substances in the working of plating solutions. There is little doubt that a great deal of research work remains to be done in that direction before we can gain full information as to what exactly happens in the various processes of electrodeposition.

In conclusion, on your behalf and my own, I should like to express our hearty thanks to those who have given papers and also to those who have contributed to the discussions.

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A FORCE FIELD DISSOCIATION THEORY OF SOLUTION APPLIED TO SOME PROPERTIES OF STEEL.

(*A Paper read before* THE FARADAY SOCIETY, *Monday, December* 20, 1920, SIR ROBERT HADFIELD, BART., F.R.S., PAST-PRESIDENT, *in the Chair.*)

BY PROFESSOR E. D. CAMPBELL,

UNIVERSITY OF MICHIGAN.

In Roberts Austen's presidential address before the Iron and Steel Institute in 1900 he states that "In 1806 we find a fundamental statement by Berthollet's countryman and courteous opponent, Proust, which is of singular interest to us. At that early date he describes cast iron as a solution of carbide of iron in iron. He cites it as a case of a compound united to an excess of one of its elements, and clearly anticipates the modern view that carburised irons are solid solutions." More than half a century later Matthiessen in England states that steel and other alloys should be regarded as solid solutions. It was not, however, until some years after Matthiessen's work that the solution theory of steel began to take definite form and to be accepted as a means of interpreting the phenomena resulting from the heat treatment of iron and steel.

The concept that solid solutions like white cast iron or hardened steel have essentially the same mechanism, that is, the same atomic relations between the solutes in solution and the solvent as exist in ordinary aqueous solutions is not fully accepted by most metallurgists at the present time. Some of the reasons for this may be traced to the persistence of several ideas.

The development of inorganic chemistry has depended almost entirely on studies of the properties of liquid aqueous solutions. As a result, the idea that the terms solution and liquid are practically synonymous still persists in the minds of many metallurgists. To them the expression "solid solution" seems to involve a contradiction of terms. The words liquid and solid are used to indicate merely two different physical states. No knowledge of chemical composition is necessary to determine whether a body is a liquid or a solid and we find all stages of differences in viscosity between a perfectly mobile liquid and a typical solid. On the other hand, any solution must be composed of at least two entities, one a solvent and the other a solute or substance dissolved. If we could obtain absolutely pure water we would have a liquid but not a solution. This liquid would become a solution only when some second substance was dissolved in it. In the same way if we had strictly pure iron it would be a solid but not a solution, since it would be composed of but a single chemical entity. As soon, however, as the iron contains any second substance, such as carbon, silicon or other element, it would become a solution just as truly as does the pure water to which a salt has been added.

A second reason why metallurgists and chemists have not been in the habit of regarding metallic solutions in the same way they do aqueous

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solutions is that in experimental work on these latter, the composition is usually expressed in molecular concentration per unit volume, whereas in metallic solutions it is customary to express the composition in weight per cent. For most scientific work the concentration of aqueous solutions is expressed in terms of molar solutions or fractions thereof. A molar solution may be defined as one which contains the molecular weight of the solute in milligrams in one cubic centimetre. The electrical conductance of aqueous solutions is usually expressed in reciprocal ohms times 10^{-6} per centimetre cubed. The electrical resistivity, thermal conductance and magnetic properties of metallic solutions for scientific work are usually expressed in appropriate units per centimetre cubed. If, therefore, we hope to determine the correlation between chemical constitution and physical properties, it would seem only logical to adopt for metallic solutions the same system of expressing the composition as is used for aqueous solutions, giving the composition in terms of volume concentration rather than weight per cent. If the percentage composition of a metallic solution such as white cast iron or steel is known, this may readily be converted into atomic concentration, that is, the number of milligram atoms per cubic centimetre, by means of applying the formula:

$$\frac{10 \times D \times \text{per cent. of element}}{\text{Atomic weight of element}}$$

where "D" is the specific gravity of the alloy, the per cent. and atomic weight being that of the element under consideration. Since the specific gravity gives the weight in grams of one cubic centimetre and the concentration is to be expressed in milligram atoms per cubic centimetre, the 10 comes in because it is first necessary to multiply by 1000 to reduce grams to milligrams and then divide by 100, due to the composition being expressed in weight per cent. If a steel had the following composition: C – 0·945 per cent., Mn – 0·189 per cent., P – 0·013 per cent., S – 0·016 per cent., Si – 0·155 per cent., the atomic concentration of the carbon would be

$$\frac{10 \times 7{\cdot}85 \times 0{\cdot}945}{12} = 6{\cdot}28 \text{ milatoms per c.c.}$$

Similarly the atomic concentration of the other elements would be: Mn – 0·27, P – ·03, S – ·04, Si – ·43 milatoms per c.c.

With comparatively little effort metallurgists, chemists, and physicists could form the habit of thinking in terms of atomic concentrations just as easily as they now do in weight per cent. If this were done many relationships between the chemical constitution and physical properties of metallic solutions would be revealed which will not be easily seen so long as compositions are expressed in weight per cent.

The iron carbon diagram with composition expressed in milligram atoms per centimetre cubed, is shown in Fig. 1. This diagram takes in all of that portion up to and including the liquid eutectic. The temperatures are given as usual on the ordinate and the composition expressed on the abscissa, the values given at the bottom of the diagram being milatoms per centimetre cubed while for comparison the corresponding weight per cents. are indicated at the top. The lettering adopted is that used in the early iron carbon diagrams and still used by most leading metallurgists. Some serious confusion in the discussion of iron carbon equilibrium has arisen from one or two writers thoughtlessly changing the arrangement of letters when discussing the iron carbon diagram,

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instead of adhering to the arrangement so long recognised in this country and abroad.

In addition to the two above mentioned reasons, namely, the confusion arising from the synonymous concept of the terms liquid and solution and the fundamental difference in the system of expressing the composition of metallic and of aqueous solutions, there is a third, probably exerting more influence on the concepts of metallurgists, physicists, and chemists than either of the two mentioned. The third reason is the very generally accepted electrolytic dissociation theory, advanced in 1887 by Arrhenius to account for chemical reaction and reactivity. The electrolytic dissociation theory was suggested as the result of researches on aqueous solutions by electrical methods. For some years prior to 1887 chemists had recognised that of all the molecules of a solute in solution only a portion were reactive, the remainder being inactive. At the time of the announce-

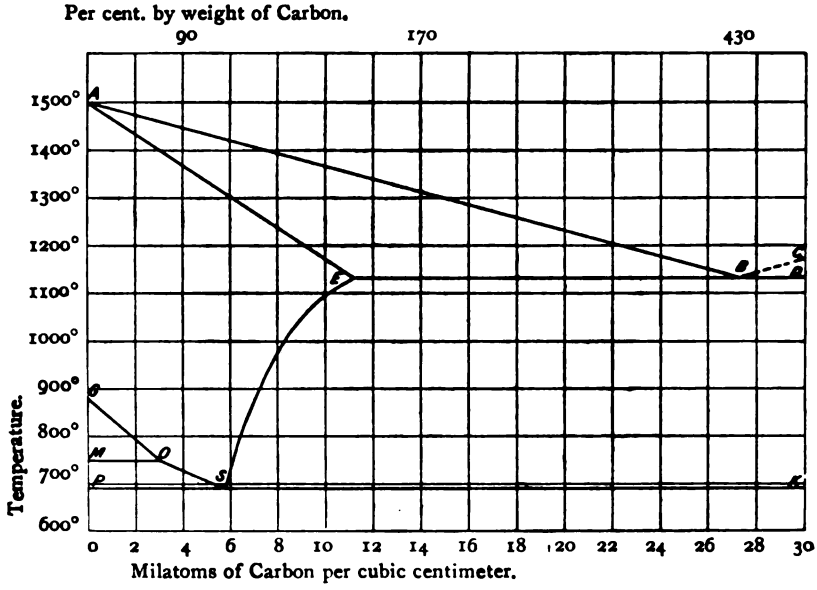

FIG. 1.

ment of the electrolytic dissociation theory, reactive molecules were assumed to be dissociated by action of the solvent into electrically charged particles termed ions. The fundamental assumption was made that chemical reaction takes place only between ions and that these ions owe their reactivity to the presence of the electric charges which they carry.

That theory of solution is most satisfactory which is capable of giving a reasonable explanation for the greatest number of known phenomena and at the same time is not inconsistent with any known facts of observation. While the electrolytic dissociation theory explains very satisfactorily many of the phenomena observed in liquid solutions where the solvent is a dielectric, it does not satisfactorily explain the behaviour of such solutions when subjected to the action of radiant energy in the form of light and is entirely untenable for metallic solutions in which the solvent is not a dielectric, but a conductor of electricity.

In 1915 in an article entitled "A Theory of Chemical Reaction and Reactivity" (*Journ. Amer. Chem. Soc.*, 1915, 979), E. C. C. Baly, as the

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result of a series of spectroscopic studies extending over more than ten years, proposed what is now known as the force field theory of solution, to account for chemical reaction and general reactivity of solutions. In the force field theory as described in the above paper the assumption is made that each atom of an element possesses an electro-magnetic force field and when two or more atoms are combined in a molecule the force field of this latter is closed. A second assumption is that when the molecule is dissolved its force field is more or less opened up by action of the solvent, the extent to which the opening takes place being dependent upon the concentration as well as on the composition of both solute and solvent. The force fields of molecules in solution which are not active are assumed to remain closed. The opening of the force fields of active molecules is stated to take place in definite steps, ionic dissociation as usually thought of not being recognized. The experimental evidence given by Baly together with that taken from the results obtained by many astronomers and physicists whose work involves a study of the action of light with both gases and liquids, seems to prove that this reactivity is primarily due to the existence in these solutions of electro-magnetic force fields. The reactivity due to these force fields will depend upon the degree to which they are opened up and the resultant of the reactions will depend upon the form of energy with which the force fields come in contact.

For the past twenty-five years the researches on the constitution of steel which have been carried on in this laboratory have been based on the fundamental concept that there is no essential difference in the atomic relations between the solutes and solvent in iron carbon alloys from those which exist in aqueous solutions. In 1899 in a paper on "The Constitution of Steel" (*J. Iron and Steel Institute*, 1899, II., p. 231), experimental evidence indicating molecular dissociation was given. In 1908 in a second article on "The Constitution of Carbon Steels" (*J. Iron and Steel Institute*, 1908, III., p. 332), the desirability of recognising the complete unity of mechanism of aqueous and metallic solutions, including ionic dissociation in the latter, was pointed out. Almost simultaneously with the publication of Baly's article on "A Theory of Chemical Reaction and Reactivity" the author submitted a paper entitled "Can the Dissociation Theory be Applied to Solid Solutions in Steels" (*J. Amer. Chem. Soc.*, Vol. 37, p. 2039). In this latter article experimental evidence is given to show that it is the products of ionic dissociation of carbides in solution which when a difference in electrical potential is established at two points, react, transforming electronic motion of electricity into atomic or molecular motion of sensible heat while conductance of the electric current takes place through the solvent iron. Thus it was shown that the products of ionic dissociation in a metallic solution are capable of reacting with electrical energy just as truly as are the ions in an aqueous solution, but the resultant of the reactivity in metallic solutions is electrical resistance, while that in aqueous solutions is electrical conductance. The reversal of phenomena, however, is not due to any difference in atomic relations between the dissolved solute and the solvent, but to the reversal in the electrical properties of the solvent. In 1915 when it had been shown that the products of ionic dissociation in both metallic and aqueous solutions are reactive with electrical energy, the author suggested that the term "ionoids" be used to define the products of ionic dissociation in a metallic solution. The term ionoid was suggested because at that time an ion was considered as necessarily carrying an electric charge, to the presence of which, the ion owed its reactivity. Baly's

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publications, which gave such convincing evidence that reactivity in solutions is primarily due to force fields rather than to the presence of electric charges on the reacting particles, clears the way for a theory which would be broad enough to include all solutions whether liquid, solid or gaseous and metallic solutions as well as those in which the solvent is a dielectric. Such a theory might properly be called a force field dissociation theory, since it would embody all the concepts now held concerning ionic dissociation with the exception of the necessary presence on the ion of electric charges to which the ions owe their reactivity. In such a theory reactivity of ions is assumed to be due to open force fields and not to the presence of electric charges, as is assumed in the electrolytic dissociation theory.

Under the force field dissociation theory, chemical reaction is assumed to take place between ions whose open force fields involve primary valences. Molecules or crystals not in solution and consequently whose force fields are assumed to be closed, may possess the property of reacting in definite ways with certain forms of energy. For instance, a liquid or a crystal consisting of a single chemical compound or of an element may react with light, that is, possess characteristic optical properties which are frequently used as a means of identification. Again, strictly pure metals react with electrical energy, that is, possess a definite electrical resistivity, which, however, obeys a different law in regard to the influence of the temperature of measurement than does the resistivity due to the reaction of the open force fields of solutes in solution in the metal. That solutes in solution possess more or less open force fields is strongly suggested by the force field existing around a pole of an ordinary magnet. The hypothesis is proposed that these magnetic force fields represent the cumulative effect resulting from the serial alignment of the poles of the force fields of carbides or other solutes in solution.

The marked difference in the electrical resistance of one milligram atom of a metal when functioning as a solvent or as a solute is strikingly illustrated by the fact that in one cubic centimetre of pure chromium the resistivity at 25° C. produced by each milatom is 0·02 microhms, whereas for the same amount of ionized chromium in solution there results not less than 3·2 microhms, an amount 160 times as great.

The relation between the electrical and thermal resistivity of pure metals has been expressed in Wiedemann and Franz's Law, but whether the same relation holds between electrical and thermal resistivity produced by the reaction of force fields of solutes in metallic solution, remains to be determined. The values reported by the author in 1917 (*J. Iron and Steel Institute*, 1917, No. II., p. 251) would indicate that this is probably not the case.

Although the microhm is the unit used to express electrical resistivity, there is at present no corresponding term for thermal resistance. Many tables are available in which the thermal conductivity of metals is given, the values showing the number of calories flowing per second through one cubic centimetre having a temperature gradient of one degree. In order to have a unit of thermal resistivity which could conveniently be compared with the microhm, the author would suggest a term "calohm" for such a unit. A calohm would be defined as that thermal resistance which would permit one calorie to pass per second through one cubic centimetre with a temperature gradient of one degree. The thermal resistivity of a pure metal expressed in calohms would be the reciprocal of the thermal conductivity. If the same relation between thermal and electrical resistivity is assumed as that on which the Wiedemann and Franz Law is based, one calohm would correspond to 10/6·5 or 1·54 microhms.

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DISCUSSION.

Dr. A. E. Oxley said that the writer of the paper divided his subject into three main parts (*a*) the inappropriateness of the term "solid solution"; (*b*) the advantage, if we are to recognise or seek a parallel between metallic and ordinary solutions, of expressing the relative proportions of solute and solvent in the same way; (*c*) the discussion of an electro-magnetic force field dissociation theory to account for the phenomena shown by liquid and metallic solid solutions.

With regard to (*a*), he thought everyone would agree that the term "solid solution" was an unfortunate one. One never spoke of a "liquid solution," and the simple term "solution" was quite adequate to cover all cases.

The point raised by Professor Campbell in (*b*) was of a more vital nature, in so far as future progress was concerned. Clearly, if the ordinary phenomena of solution in liquids and of certain elements in metals were of the same nature, or at least, if they were suspected to be so, the analogy would be most clearly brought out if the constitutions of the solutions were interpreted in the same way. With the views expressed by Professor Campbell in (*a*) and (*b*) he concurred.

It was in connection with (*c*) that the discussion was mainly concerned, and he thought that Professor Campbell's attitude was one which physicists would commend. Professor Campbell referred to the old ionisation theory of Arrhenius, put forward in 1887, and said that on this new theory which he and Professor Baly were advocating, no such electrolytic dissociation as that mentioned by Arrhenius was taken into account. Instead of having positively or negatively charged atoms and molecules, he has a simple force field, and I want to make it clear what that force field is. The modern constitution of matter as disclosed by the recent work of Sir Ernest Rutherford, is that the atom consists of a nucleus or core made up of charges of positive electricity. Surrounding this nucleus there is some special arrangement of negative charges, called electrons, and a neutral atom is simply an atom in which the sum of these negative charges is equal to the total positive charge on the nucleus or core of the atom. If by some means, either by chemical reaction, or dissolving a salt in water, or bombarding atoms, it were possible to abstract one of these electrons from the system constituting the atom, then the system would have one less negative charge than was required to make the whole system neutral, and that would correspond, on the theory of Arrhenius, to the positively charged ion. If, on the other hand, it were possible to add an electron to this system, then we should in a similar sort of way produce a system which had one more negative electron than was required by the number of positive charges on the nucleus, and we should get a negatively charged ion. In that way we could manufacture positive and negative ions which were generally admitted to occur in all electrolytic problems. If, on the other hand, we take a neutral atom, *i.e.* one containing equal numbers of positive and negative charges, it is not an ion in the sense indicated by Arrhenius' theory, but if we imagine ourselves stationed at a point in

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between a pair of such atoms it would be found that there would be a resultant force at a point close up to the atom—that might be called the force due to the stray field, and that field was the electro-magnetic force field which Professor Campbell referred to in his paper. It was an electric force and probably also a magnetic force which existed close up to the atom or molecule which might be in solution or not. In other words, it was something additional to Arrhenius' theory of positively and negatively charged ions.

With regard to the existence of an electro-magnetic force field, he agreed with Professor Campbell's view, but he did not agree with him when he spoke of the electro-magnetic force field as being itself competent to account for all the reactivity phenomena of solution. He felt that it would have to be admitted that not only were electro-magnetic force fields necessary to explain the phenomena which were observed, but that Arrhenius' had got to be admitted.

Although he could not agree with the replacement of Arrhenius' theory of charged ions by the new theory of the open or closed electro-magnetic fields without recognising in certain cases the occurrence of positively or negatively charged ions, he fully appreciated in metallurgical problems the recognition of atomic and molecular force fields in media which are unionised. This, he thought, was really the new point of Professor Campbell's paper, and he would like to say at once that the latest physical evidence shows that both conceptions are necessary to account for the known facts.

Professor Campbell quotes Professor Baly's theory and says: "In the force field theory as described in the above paper (a spectroscopic investigation as to the nature of chemical reaction and general reactivity of solutions), the assumption is made that each atom of an element possesses an electro-magnetic force field and when two or more atoms are combined in a molecule the force field of this latter is closed". If this is so it is difficult to see what the origin of the residual forces determining crystallisation can be, for if, owing to chemical combination, the force field of the molecules in a liquid is closed, there can be no inter-molecular forces which are essential for crystallisation. Later on Professor Campbell apparently evades this difficulty and says "molecules or crystals not in solution and consequently whose force fields are assumed to be closed, may possess the property of reacting in definite ways with certain forms of energy". Professor Campbell goes on to say: "Baly's publications, which gave such convincing evidence that reactivity in solutions is primarily due to force fields rather than to the presence of electric charges on the reacting particles, clears the way for a theory which would be broad enough to include all solutions whether liquid, solid, or gaseous, and metallic solutions as well as those in which the solvent is a dielectric. Such a theory might properly be called a force field dissociation theory, since it would embody all the concepts now held concerning ionic dissociation with the exception of the necessary presence on the ion of the electric charges to which the ions owe their reactivity. In such a theory reactivity of ions is assumed to be due to open force fields and not to the presence of electric charges, as is assumed in the electrolytic dissociation theory."

In connection with Arrhenius' theory of the nature of ionisation, some interesting results had been obtained in recent years from the work of Sir William and Professor W. L. Bragg as to the constitution of crystal structure. They had shown beyond doubt that in the case of metallic

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salts such as sodium chloride and potassium chloride, the crystal lattice was one consisting of positively and negatively charged ions. For example, in the case of sodium chloride they had shown that the lattice was of the simple cubic type; there were positively charged sodium atoms, each surrounded symmetrically by negatively charged ions, and each of the negatively charged ions was surrounded by positively charged ions. The same kind of structure held for potassium chloride, and, moreover, the ions which the work of the Braggs had disclosed, were of the same nature as the ions recognised by the Arrhenius' theory. Additional evidence had accumulated during the war as to the structure of these crystals. This was due to Debye and Scherrer, and confirmed the work of the Braggs, and these workers had produced evidence to show that in the case of lithium fluoride, the electron had really passed from the lithium atom into the fluorine atom, the lithium atom thereby acquiring a positive charge, the fluorine atom a negative charge, the atoms becoming ions in the sense that Arrhenius described in his theory in 1887.

With regard to the latter part of Professor Campbell's paper, where he speaks of the electro-magnetic force field, there was plenty of physical evidence accumulating which backed up the views advocated in the paper, but he wanted to make it perfectly clear that, although he agreed with that part of Professor Campbell's paper, he did not agree with him or with Professor Baly when they say that the "ionoid" theory alone is sufficient to account for the reactivity effects. It would be necessary to accept both the force field theory, and also in certain cases (as for instance, the case of the salts he had referred to), the old theory as originally put forward by Arrhenius.

There was a type of chemical combination which was different from that which he had just mentioned in the case of sodium chloride, potassium chloride, or lithium chloride, in which chemical combination appeared to be due to the transference of electrons from one atom to another. For instance, when two hydrogen atoms came together they formed a molecule, and there was some special relation between the atoms which determined a certain attractive force, even in atoms which were exactly alike, and he thought it was obvious that here they were running up against a problem which was decidedly different from that which he had mentioned in the case of sodium chloride. In this latter case they had chlorine, which was electro-negative, and sodium, which was electro-positive, and it might be expected that there was a tendency for two such atoms to combine, but they were up against a difficulty when they tried to imagine what goes on when a hydrogen atom combined with another hydrogen atom. If they imagined that the hydrogen atom, which had been shown by abundant physical evidence to consist of a single charge of positive electricity in the nucleus, with one electron spinning round it, or at any rate, displaced from it at a distance comparable with 10^{-8} cm., and if they brought up another system similar to this one with another electron in it, it was necessary to give some sort of theory which would account for the attraction of these two systems, because ionisation in a case like this, *i.e.* the transference of one electron from one atom to the other, which would correspond to the case of sodium chloride or potassium chloride, was, he thought, very unlikely. It was hardly likely, for instance, that one atom would be satisfied by taking under its control an electron which really belonged to the other atom, any more than the reverse process could take place. Therefore, it was necessary to get a different conception of the forces between the systems, and in that connection they had what

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Professor Campbell included in his term, the electro-magnetic force field, only in this case the force field was not necessarily electrostatic; it might be and probably is partly magnetic. There was a good deal of evidence gradually accumulating to show that an electron was not a simple negative charge. It was more complex than that. Possibly the electron was spinning in an orbit, in which case they had not only got the electric force due to the negative charge of the electron, but there was also magnetic force, because an electron spinning in that orbit was equivalent to a current going round a wire, so that in addition to the electrostatic effect there was a magnetic effect. Recent work seemed to be tending along the line that the electron itself is not a negative charge only but is a unit of magnetism also. If they accepted this extended view of the electron, they might, for instance, think of the combination of two exactly similar hydrogen atoms as determined by the electro-magnetic induction between a pair of small electron orbits (*a*) and (*b*) (Fig. 1). (*a*) and (*b*) may be ring

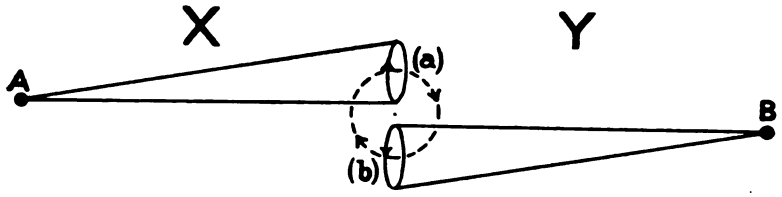

FIG. 1.

electrons forming with their respective positive nuclei A and B the neutral atoms X and Y. More complex atoms and molecules might in a similar way be imagined as built up from hydrogen atoms. They had got there big electrostatic and magnetic forces but no free charges or ionisation in the ordinary sense, and these were the forces which Professor Campbell referred to when he spoke of the electro-magnetic force field.

On the Bohr-Sommerfeld theory, which has been so successful in the interpretation of spectral series, it seemed impossible to account for the diamagnetic properties of hydrogen and helium. Hydrogen in combination behaved like a diamagnetic substance, while liquid hydrogen and liquid helium were diamagnetic. When it was considered that by far the larger portion of substances known to us were diamagnetic, it seemed that some sort of electro-magnetic coupling such as that indicated in Fig. 1 was necessary. If the coupling orbits have opposite spins, the system is diamagnetic; if the spins are in the same direction, the system is paramagnetic. In fact, on this basis it was possible to explain the behaviour of crystalline bodies suspended in the magnetic field, whether they were ferromagnetic, paramagnetic, or diamagnetic, and abundant data relating to the characteristic deportment of crystals had been supplied by Tyndall to test these views. On the Bohr-Sommerfeld theory, where the electrons were moving in large circular or elliptical orbits in the nuclear plane, it did not appear possible to account for the deportment of diamagnetic crystals in the magnetic field at all.

The electrons are probably describing very small orbits over spherical or ellipsoidal surfaces surrounding the nucleus. The electron may itself be a complex endowed with magnetic as well as electrostatic properties. In this way was secured the stationary position of the electron as a whole, the electrons being arranged in three dimensions as is required to explain the magne-crystallic properties and the crystal structure as disclosed by X-ray analysis.

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The system which has been advocated above is one in which the atoms and molecules consist of electrostatic and magnetic doublets, and in a recent paper (*Roy. Soc. Proc.*, A, Vol. 98, p. 264, 1921) he had attributed the intrinsic pressure in elements and isotropic non-conducting media to the open electrostatic doublets, whose size is of the order 10^{-8} cm., while the crystalline rigidity is due to the highly localised nature of the magnetic doublets, which are of a much smaller order of magnitude.

He thought that here we were on precisely the same ground as Professor Campbell. Whenever solution takes place, whether it is that of a salt in a liquid or of one metal or non-metal in another metal, we have to take into consideration the possible effects of these electrostatic and magnetic doublets. This is true for atoms of all descriptions whether they form parts of conducting or non-conducting substances, and whether they are ferromagnetic, paramagnetic, or diamagnetic. All atoms have comparable numbers of electrons which revolve, or appear to revolve, in orbits of comparable size, and the periods of the oscillations to which they give rise are of the same order. Hence the local electrostatic and magnetic forces to which the doublets give rise are comparable in all types of matter. In so far as reactivity with externally applied energy is concerned, it seems that such force fields must inevitably be assumed and there is abundant physical evidence derived most logically from non-conducting substances that these forces are of great importance.

He believed it would be possible to apply the force field theory with a fair amount of success in the near future to certain metallurgical problems. There had recently been developed a new theory of the chemical constitution of atoms. It was known as the Lewis-Langmuir theory, and although it originated primarily to account for chemical effects, it seemed to be exceedingly promising on the physical side also, particularly as regards the interpretation of magne-crystallic action and crystal structure. The Lewis-Langmuir theory concerns itself with the explanation of chemical combination in terms of electron theory. The first type of combination is the one which has already been discussed above in relation to sodium chloride, lithium fluoride, etc., and is one in which the process of combination is accompanied by ionisation. The second type of combination is one involving no ionisation in Arrhenius' sense, and is observable when identical atoms combine to form diatomic or triatomic molecules, or when, as in organic compounds, electro-negative atoms combine to form non-conducting compounds. Here it is not plausible that the atoms are ionised for there is no apparent reason why for example one hydrogen atom should give up its only electron to another hydrogen atom which already possesses one electron, *i.e.* as much negative electricity as it can do with. Similarly in organic non-conducting crystals it is hardly conceivable that particular atoms or molecules should give up or take up electrons from exactly similar systems. The type of interatomic or intermolecular forcive which is involved in these cases is due, on the Lewis-Langmuir theory, to the sharing of electrons, or, as it is sometimes called, the holding of electrons in common. Electrons may only be held in common in pairs and the chemical evidence, as Lewis remarks, points to the conclusion that when a pair of electrons is held in common by two atoms, these electrons appear to be specially close together. Now each electron carries a negative charge and the close approach of the electrons in the pair can, as far as we know at present, only be realised by assuming that each electron is more or less completely bound to its own nucleus electrostatically, the attraction between the electrons being determined by

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the unbalanced electro-magnetic induction which threads the orbits of the revolving electrons or which is associated with the ring electrons. In this way a balance is secured between the electrostatic and the electro-magnetic forces of the atoms or molecules, and results in an attraction between identical systems (*cf. Phil. Trans. Roy. Soc.*, A, Vol. 220, p. 276, 1920).

The pair of electrons referred to above is the most stable grouping. The next most stable arrangement is that of eight electrons arranged at the corners of a cube, and hence this theory is often called the cubical atom theory. It was imagined for instance, not that the atom was exactly a cube, but that round the positive nucleus of the atom the electrons were arranged in shells, the electron motions being localised, as opposed to the large orbital motions round the nucleus demanded by Bohr's theory. The electrons may describe small orbits about their mean positions of equilibrium and it might be that the electron itself was a little vortex, or ring, located at a definite point relative to its nucleus.

The iron atom on the cubical atom theory consists of a central positive nucleus round which are arranged 26 electrons. Two of these form a stable pair close to the nucleus and the other 24 are arranged in three groups of 8, *i.e.* at the corners of three cubes (which may be more or less distorted).

Applying this cubical atom theory to the remarkable change in the magnetic properties of iron and steels at the critical temperature, it would be seen that the crystalline structure was of the simple cubic form on either side of this temperature; below it the mutual magnetic action of the atoms or molecules was very great, but above it the action was apparently small in comparison. Preserving the same distribution of electrons within the atom, in accordance with the cubical atom theory, cubical symmetry would be obtained above and below the critical temperature. If, however, below this temperature the electron orbits or magnetons were so orientated that their local fields were additive, implying a more open force field, ferro-magnetism would be possible. Above the critical temperature the magnetons might in part be internally self-compensated, and the magnetic force would then be more highly compensated, with the result that the substance might cease to be ferro-magnetic and become para-magnetic. Some kind of effect such as this probably took place when iron and nickel formed the carbonyls $Fe(Co)_5$ and $Ni(Co)_4$, which were diamagnetic, the magnetic force field being practically closed in these compounds. There was X-ray evidence that the electron was a complex whose centre of gravity remained fixed relative to the other electrons, while it was capable of rotating about its own centre of gravity. Compton and Trousdale had examined magnetite, hæmatite, and pyrrhotite when magnetised and unmagnetised, and they came to the conclusion that the electrons, during the process of magnetisation, did not leave the positions they had before magnetisation. On the other hand, Forman had shown that there was a slightly increased absorption coefficient in iron when it was magnetised parallel to the transmitted beam. At the present moment there was a very fascinating field for research in this direction, and he believed it would be found that the so-called stationary electron itself was very complicated, and involved not only an electrostatic but also an electro-magnetic field. If so, then there was ample ground for the theory of force field which Professor Campbell was advocating in his paper. At the same time, he felt that it was not sufficient to consider merely the electro-magnetic force field alone to account for the various

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phenomena, but in certain cases we must recognise the existence also of definite negative and positive ions as they were known to the older theory of Arrhenius.

Professor A. W. Porter said he had been acquainted for some time with Dr. Oxley's views with regard to atomic constitution, especially in reference to the magnetic properties of bodies, and however sceptical some might be as to whether any of the theories in regard to the atom were really quite safe to be accepted, he felt that Dr. Oxley's views should certainly be taken into consideration along with some of the others. There were difficulties with regard to the Bohr-Sommerfeld theory which he had never been able to overcome, and he did not see that it was likely that they could be overcome, whereas Dr. Oxley's suggestions really seemed to show a possible constitution which might explain the difficult things which the others failed to explain. He quite agreed with Dr. Oxley that the old idea of ionisation could not be given up quite so easily as Professor Campbell seemed to wish them to do. It must come in, because it was impossible to explain the values of the osmotic pressure of electrolytes or ordinary electric conduction unless the existence of ions of the old type was assumed. He had no inclination whatever to follow Professor Campbell if he wished to suggest that the ionisation theory must be dismissed from consideration altogether. There were other things, however, coming into play also. Not long ago the Society held a discussion on the present state of the ionisation theory, and they knew that even that discussion did not settle everything. The difficulty seemed to be that whilst they might hold quite strongly to the old view of the existence of ions, yet they could not neglect the forces which existed between them, and the complete mathematical discussion of these forces did not at the present time seem to be possible. Indeed, the difficulty of explaining the non-satisfaction of Ostwald's law of solution had not been overcome, and the existence of forces due to the positive and negative bodies in the manner described by Dr. Oxley might have to be taken into consideration. He was not very clear how the theory would apply to ordinary ionisation, because the close fields described by Dr. Oxley would only come into play when the ions were exceedingly close together, and it seemed to him that that point needed to be thought over a great deal before the bearing of such fields upon the problem would be made clear.

Professor T. M. Lowry said that the discussion seemed to have concentrated on the structure of the atom, the molecule and the crystal, and not much had been said about the bearing of these questions on the properties of steel. One of the interesting things about this group of subjects at the present time was the way in which we were becoming most grossly materialistic in our views.

Rutherford's atoms, Langmuir's molecules, and Bragg's crystals were typical examples of modern materialism and were in pleasing contrast to the intangible doctrines of former days. To those who did not enjoy thermodynamics the change was particularly refreshing.

Mr. A. L. Norbury said there was one sentence in the paper which he found rather puzzling. Professor Campbell said "if the percentage composition of *a metallic solution, such as white cast iron* or steel, was known," etc., but he thought it was generally agreed by metallurgists that white cast iron was not a metallic solution, it was distinctly duplex under the microscope. His own paper showed, he thought, that there were certain essential differences between aqueous solutions and metallic solutions, as judged by the way in which they conducted the electric current.

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Professor T. M. Lowry said that Dr. Oxley had spoken about electrons revolving, and he seemed to have pictured a single charge running round and round in an orbit, apparently without anything to go round. Was it possible for an electron to chase its own tail in that way?

Sir Robert Hadfield said that as Dr. Oxley had referred to steel, he himself would like to say a word on that subject. The hardening of steel presented a marvellous problem. If a steel containing ·8 per cent. of carbon was heated 10,000 times, or for that matter any number of times, to 729° C., and quenched in water as many times, such steel would remain soft and unhardened. If the same steel were heated to 731° C. and quenched in water 10,000 times, every time it would be hard. That was a remarkable difference in physical properties brought about by a difference of only 2° C., and the fact had been brought home to his mind by the work of Mr. S. N. Brayshaw, of Manchester, who wrote a paper on the subject for the Institution of Mechanical Engineers some years ago, in which this remarkable difference of a few degrees in temperature was dealt with as the result of tests upon a large number of specimens of steel which he (Sir Robert) had supplied. With all due deference to the physicists and chemists, we were still in Egyptian darkness with regard to a correct explanation of the problem. Similar remarkable phenomena were noticeable with regard to the magnetic properties of steel. At a certain temperature it was magnetic, but a few degrees beyond that it became practically non-magnetic. He was very much interested in the remarks of Dr. Oxley with regard to steel, because of his own early experiments upon manganese steel. A steel containing 87 per cent. iron 12 per cent. manganese and 1 per cent. carbon was absolutely non-magnetic, and the only way of making it magnetic was to heat it for a long time, many hours, at a low temperature, about 500°. The material then became quite strongly magnetic, and retained about 60 or 65 or 70 per cent. of specific magnetism, as compared with pure Swedish charcoal iron. If that same sample, however, was reheated to about 800° it again became absolutely non-magnetic. The addition of 12 per cent. manganese and heating to that temperature gave a non-magnetic product. Another alloy of his (Sir Robert's) which Dr. Oxley was investigating at the present time had a very peculiar composition. With only 5 per cent. of manganese and 1 per cent. of carbon the material was intensely magnetic, but with 5 per cent. of manganese, 14 per cent. of nickel, 1 per cent. of carbon, and 80 per cent. of iron the material was non-magnetic, so this peculiar quality did not entirely depend upon the percentage of manganese. Dr. Oxley was able, with his very exact testing apparatus to test the special alloy containing nickel and manganese and detect the not very high magnetising forces, but practically speaking it was non-magnetic. In some respects this alloy was more marked than ordinary manganese steel, but it could not be changed in the same way that the manganese steel could by heating, so that it was not reversible in that sense.

Professor T. M. Lowry asked if that was due to the use of four components instead of three.

Sir Robert Hadfield said it had no doubt something to do with the structure, and demonstrated how complex the problem was. With reference to the term "solid solution," he agreed with Dr. Oxley that it was a misleading one. It had misled him on a number of occasions, and he never could quite understand what was really meant. That might b due to his ignorance, but he was glad to find Dr. Oxley did not agree with it, and the sooner it was dropped the better. He need hardly say that

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any suggestions put forward by Dr. Oxley were worthy of consideration. He knew of no one who had a more important field of research open to him than Dr. Oxley, and he wished him every success.

Mr F. S. Spiers asked whether Dr. Oxley's theory of the atom explained the spectra series.

Dr. Oxley replying to the discussion said, in answer to Professor Lowry, that an electron projected at right angles to a magnetic field would be curled up by the latter into a circular orbit of radius $\frac{mV}{He}$, where V is the velocity of projection, H the intensity of the field, and e and m are the charge and mass of the electron. The frequency of revolution is given by $\nu = \frac{He}{2\pi m}$ and this does not depend on the speed of projection. Such a view, however, provides no explanation of the permanency of the orbit. If the electron were a vortex of negative electricity, it would still, assuming its motions to be governed by Newtonian mechanics, lose energy on account of repeated accelerations. The only way out of this difficulty seemed to be the assumption that the electron obeyed non-Newtonian laws and it was conceivable that quantum relations similar to those advocated by Bohr might apply to the electron. It was becoming more apparent that the electron consisted of something more than a negative charge. The tracks of β-particles, as shown by C. T. R. Wilson's stereoscopic photographs, have a decided spiral character, and this can be accounted for if we assume the β-particle to be a magnetic doublet which passes through or near atoms containing similar magnetic doublets. The gyroscopic right- or left-handed deviation of the β-particle is a differential effect determined by the closer approach of the striking and struck magnetons when their axes are in the same direction as compared with the greater separation when the axes are opposed. The deviation of the β-particle will be greater in the former case than in the latter, and the right- or left-handed nature of the resultant spiral will depend on the initial orientation of the axis of the β-particle. MaLaren had calculated the angular momentum of an ætherial vortex and found it to be $\frac{1}{8\pi^2} \cdot Ne \cdot Nm$ where Ne is the number of electrostatic tubes terminating on it, and Nm is the number of magnetic tubes threading it. The stability of such systems was an unknown quantity at present. Dr. Borns had raised the question of the stability of the systems of electrons used in the cubic atom theory, *viz.* the electron pairs and octets. Parson has shown that the octet formation is one of minimum magnetic potential energy and the electron pairs would be stable astatic systems.

Sir Robert Hadfield had referred to the hardening of steels, and it was an extraordinary fact that such a fine range of temperature, two or three degrees, would repeatedly produce this effect. But he did not think that this effect was more remarkable than that which took place during cooling or other substances. A liquid under a definite pressure has a definite melting point. If the crystalline form were heated to a point just below the melting point, and then cooled, it remained crystalline, but if it were heated to a point just above the melting point and cooled, a supercooled liquid or a jelly could repeatedly be obtained.

Sir Robert Hadfield said that it still remained a solution all the time and it was difficult for the human mind to think of some of the extraordinary changes going on in a steel when it was heated and became a liquid and was then cooled down.

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Dr. Oxley, speaking with regard to the magnetic properties, said he had investigated the properties of some of the so-called non-magnetic steels and had been using an apparatus which measured susceptibilities of the order of one ten-millionth, and in every case he had found the specimens decidedly paramagnetic. With the methods ordinarily used to measure the magnetic properties of non-magnetic steels they would be said to be non-magnetic but they had, nevertheless, got a slight paramagnetic susceptibility. An interesting fact was that the magnetic properties of iron varied so enormously, and he would like to refer to one or two simple cases of chemical combination in this connection. For instance, if they took iron which was ferro-magnetic, they could combine it with carbon monoxide to form the carbonyl $Fe(CO)_5$, and in the same way, if they took nickel which was ferro-magnetic, it was possible to form the carbonyl $Ni(CO)_4$, and the susceptibilities of both compounds were about equal to that of water. Another case was copper sulphate; copper was diamagnetic, cupric salts were paramagnetic, while cuprous salts were diamagnetic. If in alloy steels definite intermetallic compounds were formed, there was every reason to suppose that these chemical combinations determined quite new magnetic properties in general.

With regard to the question of Mr. Spiers, he was afraid that the explanation of spectra was a difficult one. The answer would at present have to be vague. It was possible, as had been stated above in reply to Professor Lowry, that the quantum relations might eventually be found applicable to the complex electron unit. Langmuir, in his cubical atom theory, supposed that the electrons oscillated about certain fixed positions which formed the corners of a cube. The theory which had been most successful spectroscopically was that of Bohr and Sommerfeld but apparently this would explain only the very simplest cases when the atomic system contained an isolated electron or when the system was such that the effects of other electrons could be omitted. If, as was known from optical work, the electrons were in motion with definite periods, then when the atoms containing such systems were very close together, it would be necessary to take into account not only the electrostatic but also the magnetic forces between the electron systems. In other words we must recognise the existence of electro-magnetic force fields, but superimposed on these there must in certain cases be a recognition of Arrhenius' old theory of positive and negative ions.

Professor E. D. Campbell (*reply received March* 16, 1921).

Dr. Oxley evidently feels "that it was not sufficient to consider merely the electro-magnetic force field alone to account for the various phenomena, but in certain cases we must recognise the existence also of definite negative and positive ions as they were known to the older theory of Arrhenius".

Professor Porter stated that "he had no inclination whatever to follow Professor Campbell if he wished to suggest that the ionisation theory must be dismissed from consideration altogether".

It was because the author realised, from the beginning, that it was not sufficient to consider merely the electro-magnetic force fields alone, as was done by Baly, but that the concept of ionic dissociation must be retained and that, in special cases, as in aqueous solutions, the ions would carry electric charges, to the presence of which certain properties of the solutions were due, that he proposed the "force field dissociation theory". It was his intention to indicate by this term the retention of what seemed to be the essential ideas of both of the older theories.

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Under the force field dissociation theory, when the molecule of an electrolyte is dissolved in water the molecule undergoes dissociation into ions possessing open force fields, through means of which part at least of the energy required for dissociation is transformed into and retained on the ions in the form of electric charges. The presence of an electric charge is not essential to the existence of an ion, but is the result of ionic dissociation taking place under special conditions. Under the force field dissociation theory, in aqueous solutions, an ion, because of its open force field, possesses the power of acquiring energy in the form of electric charges, which, however, may be transmitted to other like ions, so that in conductance in aqueous solutions it is not necessary to conceive of a given ion having to travel all the way from one electrode to the other in order to transport the electric charge which it carries.

The force field dissociation theory would also suggest an explanation for the transformation, in growing plants, of the radiant energy, received by them, into chemical energy. Many biochemical reactions will probably be found to involve forces which are distinctly more magnetic than electrical. The optical properties of crystals, whether organic or inorganic, may be understood as well as the optical properties of solutions, such as glass.

If the author, in order to be in strict accord with well-known facts in metallography, had made the phrase to which Mr. Norbury refers, read—a heterogeneous conglomerate of solid solutions such as white cast iron—it might have been clearer and avoided the criticism on this point.

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THE ELECTRICAL RESISTIVITY OF DILUTE METALLIC SOLID SOLUTIONS.

By A. L. Norbury, M.Sc. (University College, Swansea).

(*A Paper read before* The Faraday, Society, *Monday, December* 13, 1920, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

Introduction.

It is not possible to obtain very much theoretical knowledge from the study of alloys in which the components are mutually insoluble, for, as the work of Matthiessen (29) some sixty years ago showed, in these systems electrical conductivity is usually practically a linear function of the composition. In systems, however, where solid solutions are formed, very much more interesting results are obtained. Small additions of solute cause a relatively enormous increase in the electrical resistivity of the metallic solvent.

In the case of aqueous solutions, definite laws governing the effect of the solute on the solvent have been discovered and are now well established. Only a very superficial analogy exists, however, between aqueous solutions and metallic solid solutions, and little is known of the laws governing the effect of a solute on a metallic solvent.

Studying this question from the electrical resistivity point of view, Benedicks (2), in 1901, put forward the hypothesis that equiatomic quantities of foreign elements dissolved in iron increase the electrical resistivity to the same amount. In a recent paper (32), however, it was shown that this hypothesis is not borne out by more recent work, which indicates on the contrary that equiatomic quantities of foreign elements dissolved in iron do not increase the resistivity to the same amount. Nickel and cobalt, for instance, have markedly lower atomic effects than any of the other elements quoted.

The present interpretation of the subject is essentially of a qualitative nature. In order to attach an accurate quantitative significance to the data quoted, for purposes of inter-comparison, it is necessary to estimate the exact significance of various relatively minor factors.

The paper is divided into three sections. In the first, the general interpretation of resistivity data is discussed.

In the second section, resistivity data relating to various dilute metallic solid and molten solutions are tabulated and plotted.

In the third section the general significance of the results is discussed.

1. General Interpretation of Electrical Resistivity Data.

Very good accounts of the historical and general aspects of the present subject are given by Guertler in his numerous papers. (Also by Broniewski (6).)

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a. Mutually Insoluble Components.

Le Chatelier's interpretation of Matthiessen's results obtained for this type of binary alloy system was that if the electrical *conductivities* of the alloys are plotted against their percentage compositions, the results lie on a straight line. Roozeboom and Guertler, however, raised objections to this and showed that in some cases it appeared as if a more linear relationship was obtained by plotting electrical *resistivity* against composition.

Working on the same problem, Schleicher (40) "made experiments to determine the influence of the mechanical arrangement of the constituents in a conglomerate on the electrical conductivity. In one series amalgamated copper wires were threaded through a glass tube and the spaces between them filled with mercury. In such a composite mass the conductivity is a linear function of the composition by volume. In the second series short lengths of amalgamated copper were placed in a tube and this was filled up with mercury. In this case the resistance of the mass is a linear function of the composition by volume. The latter condition approaches more nearly to the state of things occurring in alloys which consist of conglomerates."[1] It is thought, however, that Schleicher's second series represent an extreme, rather than a typical case of metallic conglomerates. A similar explanation to that suggested by Edwards for the copper-bismuth alloys, probably applies to a certain extent in the above case. Edwards (12) says: "With the addition of comparatively small quantities of bismuth" (to copper) "the conductivity rapidly falls to the value for bismuth. This, however, is due to the fact that the crystals of copper become completely surrounded by bismuth, and when this occurs the resistance of the mass is virtually governed by that of the element which exists at the boundaries of the crystals." Moreover, the fact that copper amalgamates so readily with mercury indicates that there is a certain "affinity" between the two and consequently, from the general conclusions arrived at in the present paper, one would expect an increased resistivity in the amalgamated layers.

In Fig. 1 the curve (*a*) represents the calculated resistivity values for copper mercury conglomerates, assuming Le Chatelier's linear *conductivity*-composition relationship (Schleicher's first series). The dotted line (*b*) represents *resistivity* as a linear function of the composition (Schleicher's second series).

That Schleicher's second series of conglomerates does not represent a universal condition in conglomerate alloys is shown by Stepanow's (44) results for magnesium-tin alloys reproduced in Fig. 2. The compound Mg_2Sn exists throughout and behaves like a pure component.

In Fig. 2*a*, the lines *a'b* and *bc'* indicate that two nearly linear conductivity-composition relationships exist between the three components: *a'* = solid solution of Mg_2Sn in magnesium, *b'* = Mg_2Sn, and *c'* = solid solution of Mg_2Sn in tin.

It is thought that a great advantage in plotting the results as resistivities is that a correct idea of the variations due to experimental error is obtained. Conductivity values, on the other hand, give a fictitious idea.

In Fig. 2*b* a comparison of the two resistivity curves meeting in a peak at Mg_2Sn, with the two possible types of curves (*a*) and (*b*) in Fig. 1, indicates that conductivity, much more nearly than resistivity, is a linear function of the composition in this particular case. The fact that

[1] *Journal of the Institute of Metals*, 1913 (i), p. 222. (Abstract.)

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conductivity is more nearly a linear function of the composition than resistivity, is also indicated in Stepanow's (43, 44) results for the magnesium-lead and other systems.

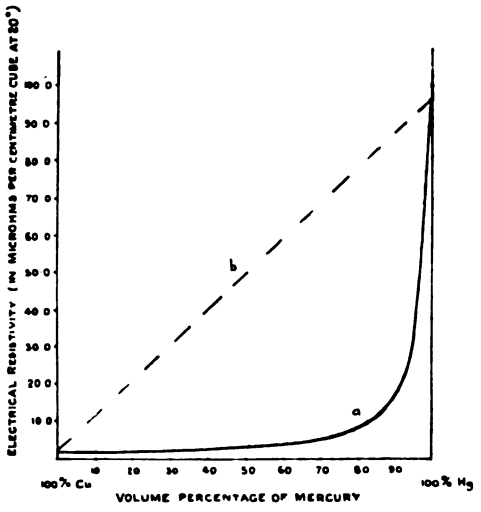

FIG. 1.—Resistivity-Composition Curves Calculated for Copper-Mercury Mixtures.

a. Assuming *Conductivity* is a linear function of the composition.

b. Assuming *Resistivity* is a linear function of the composition.

It seems probable that each crystal grain in a mechanical mixture may be considered as a separate conductor. In so far as the arrangement

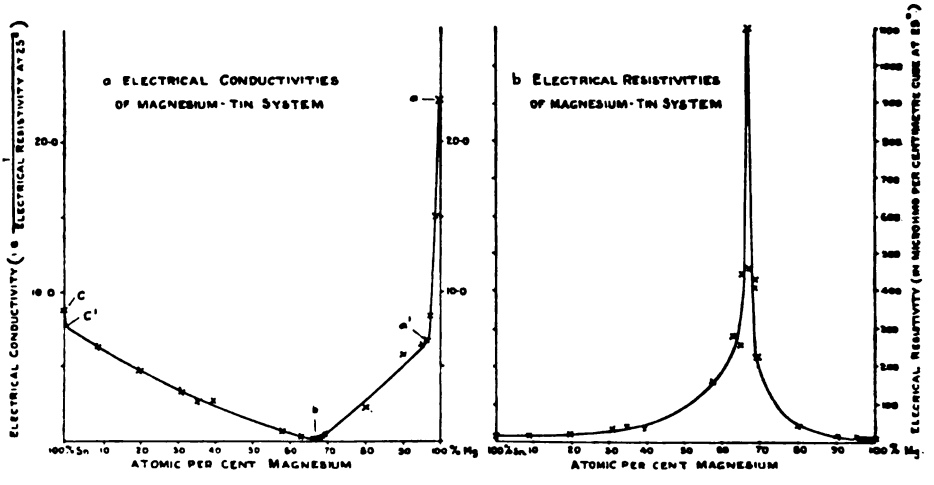

FIG. 2.—Magnesium-Tin System.
(From Stepanow, *loc. cit.*)

of the crystal grains tends to be in the nature of a number of conductors arranged in *parallel*, the *conductivity* will tend to be a linear function of the composition. In so far as the arrangement of the crystal grains

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tends to be in the nature of a number of conductors arranged in *series*, the *resistivity* will tend to be a linear function of the composition (see also section 1*e*). Every intermediate condition between the two ideal types seems possible in alloys made up of two mutually insoluble components.

b. Mutually Soluble Components.

Types of resistivity-composition curves for two components that are mutually soluble and form a continuous series of solid solutions are shown in Fig. 3.

Guertler proposed the following formula for calculating resistivity-composition curves of the above nature: He says (*loc. cit.*) "We can consider the resistance R of a solid solution as being made up of two parts, of which R_1 = original resistance *a priori*, and R_2 = solution resistance due to solid miscibility". For R_2 he gives: "$R_2 = K.C(1\text{-}C)$,

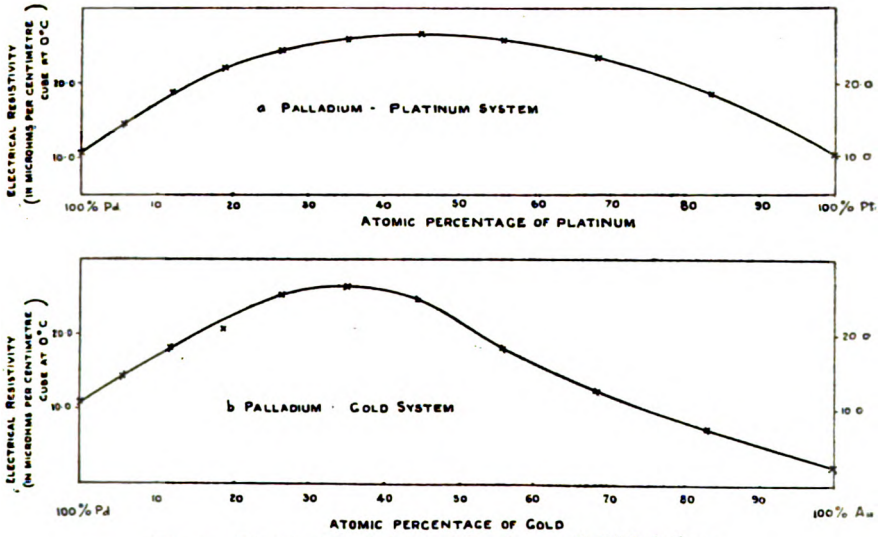

FIG. 3.—Electrical Resistivity of Continuous Solid Solutions.
(From Geibel, *loc. cit.*)

where C is the concentration of one component, and K is a constant for the series".

The assumption that R may be considered as being made up of the two quantities $R_1 + R_2$ is made from considerations regarding the effect of temperature. Temperature influences the resistivities of solid solutions in such a way that they behave as if their resistivities were made up of two independent quantities R_1 and R_2 as above, of which R_1 is strongly influenced by temperature while R_2 is practically uninfluenced (see Section 1*d*). This method of treatment appears to yield approximately correct results at all events. Assuming that this is so, a difficulty arises in calculating R_1, if the component metals have very different resistivities. It is not known to what extent the atoms in a solid solution (supposing complete mutual indifference) would partake of the nature of a number of conductors arranged in series or in parallel, or how the resistivities of such atomic mixtures would have to be calculated.

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By making certain assumptions and working backwards it appears as if mixtures of the above type would approximate more nearly to the conductivity-composition linear relationship than to the resistivity-composition linear relationship. This difficulty only arises, however, when the two component metals have decidedly different resistivities. In many cases the value of R_1 is, relatively speaking, not very important.

The two types of curve, the symmetrical and the unsymmetrical, reproduced in Fig. 3, appear to be typical of simple continuous solid solutions. The curve shown in Fig. 3*b* indicates, it is thought, that Guertler's type of formula is not sufficiently general. By having only one constant K for a binary system he assumes that the R_2 curve is symmetrical on either side. It would appear from Fig. 3*b*, however, that each component requires a separate constant K of its own.

Curves of the simple types shown in Figs. 3*a* and 3*b* may be calculated by making certain assumptions of the above nature. It does not seem probable, however, that many curves for continuous solid solutions will admit of calculation by any simple formula. Further complications usually arise due to the formation of intermetallic compounds or the partial precipitation of one of the components from solid solution. The former case is shown in Kurnakow's (27) resistivity data for the copper-nickel solid solutions, where a discontinuity at about 50·0 atomic per cent. is apparent. The latter case is shown by Kurnakow's (28) work on concentrated copper-gold solid solutions where annealing at certain temperatures was found to precipitate one of the components from solution.

The point, however, which it is wished to make at present, is that (apart from complications of the above-mentioned nature) these resistivity curves for continuous solid solutions are of a fairly simple mathematical character. Moreover, the typical constants K_A and K_B for each component, from which the whole of the R_2 curve may be calculated, are approximately represented by the initial resistivity increases on either side.

Assuming that $R = R_1 + R_2$, it will be seen that if the solute has a higher resistivity value than the solvent, the initial resistivity increase will tend to represent too large a relative value for the constant K. Conversely, if the solute has a lower resistivity value than the solvent, the initial resistivity increase will tend to represent too low a relative value for the constant K in this case. In view of the fact that R_1 seems to approximate more nearly to the linear conductivity composition relationship, it will be seen that cases in which the solute has a higher resistivity than the solvent will yield more approximately correct values by the above method of interpretation than will the converse cases. All the data quoted in the present paper refer to cases in which the solvent metal has a relatively low resistivity value. Consequently, the difference between the resistivities of the solvent and solute is often small enough to make corrections of the above nature so relatively small (in comparison with the magnitude of the solution resistivity R_2) that they are within the limits of experimental error of the figures quoted. It is obvious, however, that corrections of the above nature must be made in order to obtain values which can be compared quantitatively.

c. The Initial Addition of Solute in Dilute Solid Solutions.

Reasons for thinking that the initial additions of solute cause an almost linear (as represented by the tangent to the initial stages of the curve) increase in the resistivity of the solvent, have been given in the preceding

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sub-section. This linear type of relationship has been found in all the experimental results examined so far, with only one or two exceptions of the following type. For instance, in the cases of the copper-arsenic and copper-antimony dilute solutions a slightly concave upwards type of curve is usually obtained. The form of this curve is reminiscent of curve *a* in Fig. 1 and is thought to be due to the same cause, namely, duplexity of structure, in this case in the solid solutions. This is in accordance with the cored structures observed under the microscope.

A typical normal case showing the usual linear nature of the initial resistivity increase is reproduced in Fig. 4, where Clay's (11) results for dilute solutions of silver in gold, measured at various temperatures, are plotted.

d. The Effect of Temperature.

The general truth of Guertler's deduction "that the solution resistance" (R_2, see Section 1*b*) "does not vary with the temperature" is confirmed by

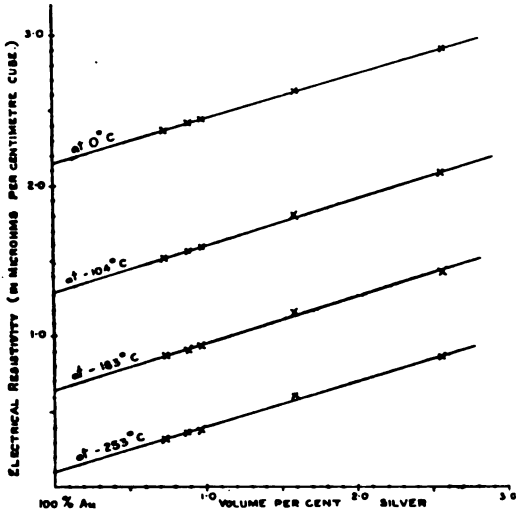

FIG. 4.—Electrical Resistivity of Dilute Solid Solutions of Silver in Gold. (From Clay, *loc. cit.*)

Clay's figures plotted in Fig. 4. It will be seen that the slope of the resistivity-composition lines is the same when measured at 0° C. as it is when measured at − 104° C., − 183° C., and − 253° C. If the solution resistivity is affected by temperature, the effect must be very small and would require exceedingly accurate measurements to detect it in this particular case.

In comparison, it will be noted that the resistivity of pure gold varies from 2·15 microhms at 0° C. to 0·09 microhm at − 253° C. At still lower temperatures Kammerlingh Onnes has found that pure metals exhibit a "super-conductivity".

There appear to be indications, however, that the solution resistivity is not altogether independent of temperature, even in solid solutions. In cases of solid solutions quoted in Section 2, where measurements on the same alloys were made at, say, 0° and 100°, a slight variation in the value

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of the solution resistivity is sometimes discernable. In Fig. 6 it will be seen that the values for various elements in solid and molten solution in copper are by no means identical, and Bornemann's (3, 4, 5) other data indicate that temperature undoubtedly affects the solution resistivity values in the case of molten alloys. In the case of solid solutions, however, the influence appears to be relatively very small, unless temperature has the effect of altering the amount of solute in solution, or altering the relative arrangement of the atoms in the alloy in any way. The solid solutions quoted in Section 2 were in all cases measured at temperatures lying between 0° and 30° and for this range the effect of temperature on the solution resistivity appears in all cases to be within the limits of experimental error.

e. The Effect of Cold Work and Grain Size.

The following figures[1] illustrate the relatively small effect of cold work, and incidentally of grain size, on the electrical resistivity of pure metals:—

	Silver.	*Copper.*	*Gold.*	
Annealed:	1·47	1·56	2·04	Electrical resistivity in microhms
Hard drawn:	1·62	1·62	2·08	per centimetre cube at 0° C.

A still more striking instance is given by Campbell (9) for iron. He found that the effect of drastic cold-hammering on annealed, pure iron (carbon 0·04 per cent.), was to increase the Brinell hardness from 76 to 240 whereas at the same time the electrical resistivity only increased from 10·50 to 10·63 microhms per centimetre cube.

Apart from the other effects of cold working, the difference in grain size between the worked and the unworked specimens would be very great, the attendant small alteration in electrical resistivity is consequently the more noteworthy.

That the effect of cold work on the resistivity of solid solutions is similarly very small is shown by Münker's data (31). Although the effect of grain size is small in the case of pure metals, it becomes more important in the case of duplex alloys and increasingly so as the degree of dispersion of the components increases. At the crystal boundary between a crystal grain of metal A and a crystal grain of metal B, in a duplex alloy, there must presumably exist a region where atoms of A are adjacent to atoms of B. It seems reasonable to suppose, therefore, that a large but local increase in resistivity will take place at such a crystal boundary, just in the same way as it does in solid solutions where atoms of A and atoms of B are adjacent to one another. The grain size in a duplex alloy has, however, to become exceedingly small before the number of the atoms comprising these crystal boundaries becomes comparable with the total number of atoms present. When, however, this degree of dispersion is reached, the resistivity increases very rapidly.

It is thought that this point is well illustrated by the progressive fall in resistivity which takes place on tempering martensitic steels at progressively higher temperatures. Temperature has the effect of causing a progressive diminution in the degree of dispersion of the carbides—consequent on coalescence—and the electrical resistivity falls correspondingly. The reason that this coalescence takes place so readily is thought to be that, whereas in austenite the carbon is in true solid solution in the γ-iron,

[1] *Metal Industry Handbook*, 1920.

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in martensite it is equally highly dispersed but is not in solid solution in the α-iron. If the quenching is sufficiently rapid the $\gamma \rightarrow \alpha$ change, and consequent precipitation of the carbide from solution, does not take place until the system has practically reached the temperature of the quenching medium. At this temperature the very highly dispersed (probably atomically dispersed) carbon atoms are thrown out of solution. Although they have a strong tendency to approach one another and coalesce, they are unable to move owing to the fact that they are wedged in between the iron atoms, for at this low temperature the system has not sufficient inter-atomic mobility to permit the necessary atomic rearrangement to take place. The fact that the dispersed system is metastable and that the carbon atoms—with attendant iron atoms—are trying to approach one another and coalesce is clearly shown by the readiness with which this takes place when the temperature—and consequently the inter-atomic mobility—is slightly raised. Campbell (9) has shown that tempering at 100° causes a very large drop in the resistivities of martensitic carbon steels; and finds that the resistivities are slowly dropping in some cases even at ordinary temperatures (10). In austenitic steels, on the other hand, in so far as the carbon is in true solid solution in γ-iron, it does not coalesce on tempering until the temperature is sufficiently high to cause first of all the austenite → martensite (*i.e.* the $\gamma \rightarrow \alpha$) transformation to take place.

The conclusions arrived at in what precedes are in some cases incomplete, but it is thought that they give a general working idea of the relative importance of the various factors which go to determine the resistivity of a solid solution. In comparison with most of the factors already discussed the influence of 1·0 atomic per cent. added element entering into solid solution is relatively very large.

2. Collection and Discussion of Experimental Data Showing the Atomic Effects of Various Elements on the Electrical Resistivity of Certain Metals.

In the present section experimental data dealing with the electrical resistivity of various dilute metallic solid and molten solutions, are collected. They have been interpreted in the light of the generalisations discussed in the preceding section.

Composition is expressed in atomic percentages, and specific resistivity is defined throughout in microhms per centimetre cube. The exact temperature of measurement is relatively unimportant from the present point of view—as has been discussed in section 1*d*—but was, in all the cases of the solid solutions quoted, somewhere between 0° and 30°.

It would take up too much space to give a detailed account for every set of experimental determinations of the methods used and the probable accuracy of the results in each case. An attempt to indicate the possible experimental errors has, however, been made by giving, in the columns showing "Increase in resistivity due to 1·0 atomic per cent added element," a maximum and a minimum possible value, deducible in doubtful cases from an investigator's plotted results. Furthermore, the "Remarks" columns show the number and the compositions of the alloys from which the above mentioned maximum and minimum values have been calculated. By taking into account the details given in these two columns, a good idea

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may be obtained of the probable accuracy of the value obtained from each set of experimental determinations.

As an illustration of the way in which the figures showing the "increase in resistivity due to 1·0 atomic per cent. added element" were actually obtained, Clay's results in Fig. 4 may again be utilised. It will be seen that the addition of 1·0 per cent. by volume of silver has raised the specific resistivity of the gold from 2·15 to 2·45 microhms at 0° C. This amounts to an increase of 0·3 microhm for 1·0 atomic per cent. of silver (since the atomic volumes of gold and silver are approximately equal). In some cases—as for example in most of the data quoted from Geibel's papers (13, 14) on palladium and platinum solid solutions—there are no figures given for very dilute solid solutions. Since, however, these solid solutions are more or less continuous, it is possible to deduce the initial increase by interpolation from the experimental values obtained for more concentrated solutions. Cases in point are shown in Figs. 3*a* and 3*b*. All the other values quoted have been interpreted in an exactly similar way and represent the difference between the resistivity of a 1·0 atomic per cent. solid solution and the resistivity of the pure solvent.

a. Solid Solutions in Iron, Nickel and Cobalt.

The solid solutions in iron shown in Table 1 have been taken direct from the previous paper (32). These data (Table I.) are shown diagrammatically in Fig. 5*a* where the atomic resistivity increases are plotted against the positions the added elements occupy in the Periodic Table.

In three cases (*e.g.* Al, Cu, Au) the solute has a decidedly lower resistivity than the solvent; the values for these three elements are therefore (for reasons discussed in Section 1*b*) to be considered as being somewhat lower than they really would be if they were calculated to a more strictly comparable basis. Apart from this, however, it will be seen that the two elements cobalt and nickel—in the same group and period as iron—have markedly lower atomic effects than any of the other elements quoted. Further, cobalt has a smaller effect than nickel. The largest atomic effects are caused by elements in the most distant groups, while the elements in the intermediate groups have more or less intermediate effects. The nitrogen and vanadium values are doubtful and, especially in the case of nitrogen, are probably too low. The manganese value is probably fairly accurate, but is considerably higher than would have been anticipated in view of the general relationship brought out more clearly in Figs. 6 and 7.[1] The nickel alloys collected in Table 2*a* and plotted in Fig. 5*b* show the same general relationship, and it will be seen that the value showing the effect of manganese on nickel is much more "normal".

b. Solid Solutions in Palladium and Platinum.

In Tables II.*c* and II.*d* some palladium and platinum alloys, which are plotted in Figs. 5*c* and 5*d*, are shown. It will again be observed that the elements palladium and platinum, in the same sub-group (8*c*), have smaller effects on one another than any of the other elements shown. As

[1] In view of the general explanation of the results suggested in Section 3, however, it is noteworthy that manganese has such a marked power of retaining iron in the γ form, indicating that some strong forces must be operating between the two. Similar remarks probably apply to some of the other iron alloys.

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a matter of interest, Wolf's (47) data for the palladium-hydrogen alloys have been calculated to the same basis, and give the relatively high value of 16·0 microhms for the atomic effect of hydrogen. This case is, however, not necessarily strictly comparable.

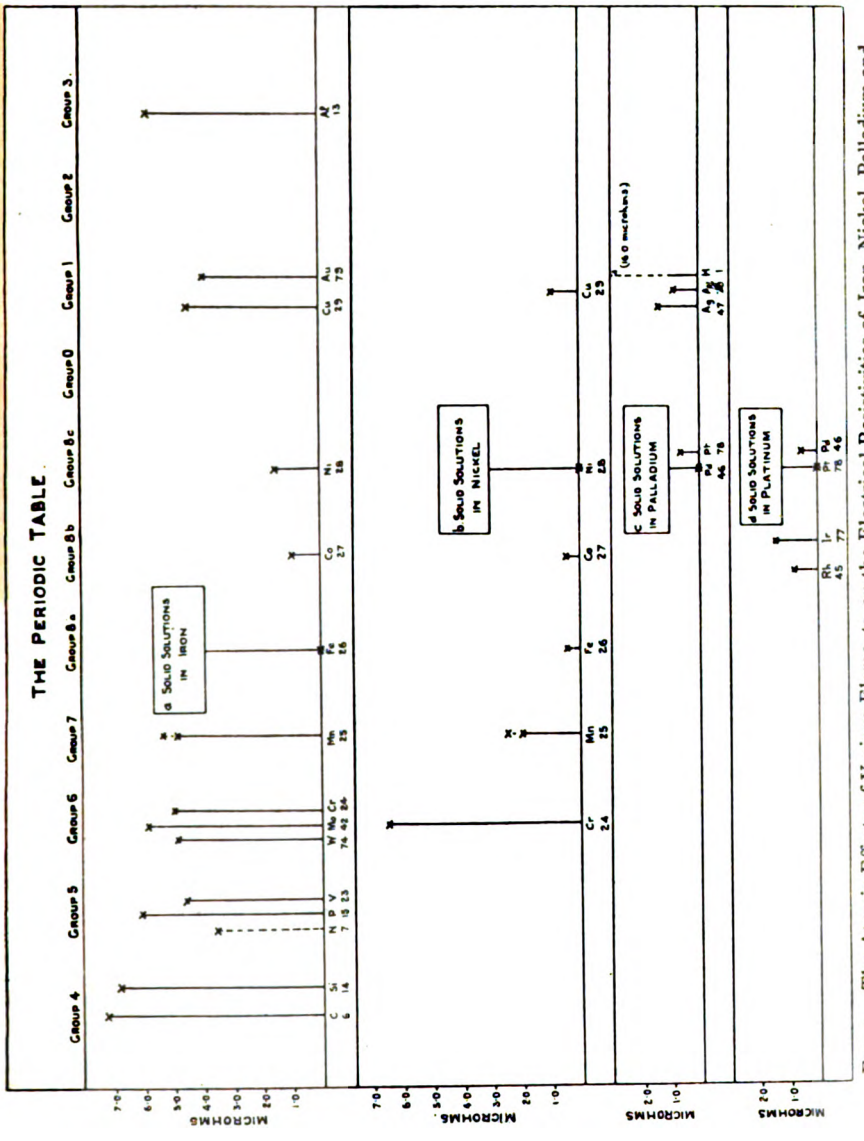

FIG. 5.—The Atomic Effects of Various Elements on the Electrical Resistivities of Iron, Nickel, Palladium and Platinum. (Tables I. and II).[2]

(The uprights indicate: Increase in the Resistivity of the pure Solvent (in microhms per centimetre cube) due to the Presence in Solid Solution of 1·0 Atomic per cent. Added Element.)

c. Solid Solutions in Copper, Silver and Gold.

In Table III. data relating to solid solutions in copper are collected. In column 4*a* of this table the effect of 1·0 per cent. by weight added element is also given. The atomic effects are plotted (thus ×) in Fig. 6.

It will be seen, on studying the results, that they ought really to be

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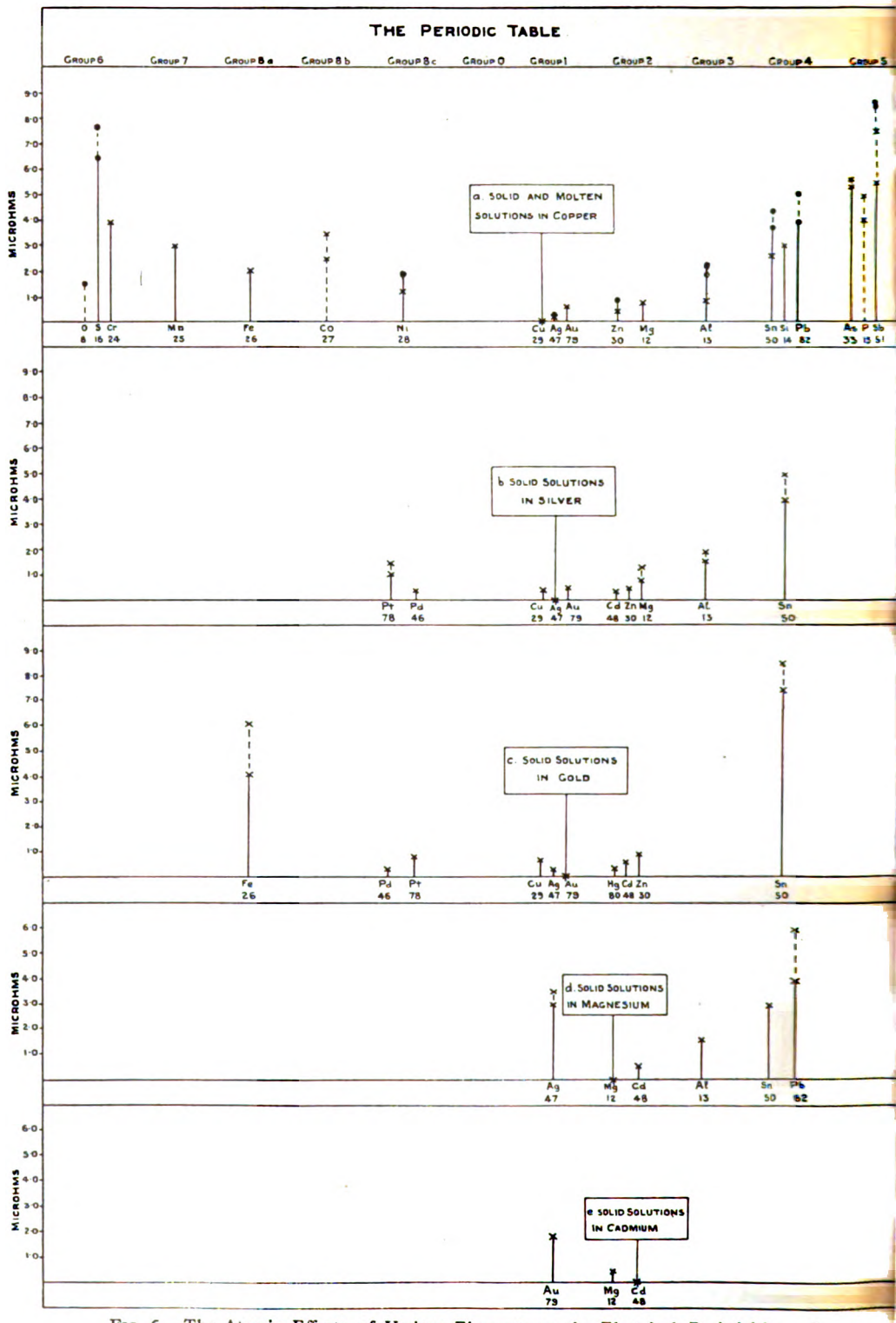

FIG. 6.—The Atomic Effects of Various Elements on the Electrical Resistivities of Copper, Silver, Gold, Magnesium and Cadmium. (Tables III. to V.)

(The uprights indicate: Increase in the Resistivity of the pure Solvent (in microhms per centimetre cube) due to the Presence in Solution of 1·0 Atomic per cent. Added Element. Solid Solutions thus x, Molten Solutions thus ● at 1100°—1400°.)

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plotted in three dimensions, the dimension not indicated being that showing the vertical arrangement of the elements in the Periodic Table. In order, however, that the vertical positions may be more readily imagined, the atomic numbers are written in under each of the solute elements. The same remarks apply also to the silver solid solutions (in Table V.*a* and Fig. 6*b*) and the gold solid solutions (in Table V.*b* and Fig. 6*c*).

Considering the plotted results in Figs. 6*a*, 6*b*, 6*c*, it is interesting to study the remarkably close relationship existing between the magnitudes of the atomic effects and the distances (horizontal and vertical) separating the solute from the solvent in the Periodic Table.

The horizontal relationship is well brought out in all the plotted results. The effects, however, of Cr, Mn, Fe, Co (doubtful, see Table III.), Ni, Zn and As on Cu are already sufficiently regular to indicate that exact values would be very interesting.

The vertical relationship is best brought out by comparing the relative effects of:—

i. (*a*) Au and Ag on Cu; with (*b*) Au and Cu on Ag; with (*c*) Cu and Ag on Au.
ii. (*a*) Mg and Zn on Cu; with (*b*) Mg, Cd and Zn on Ag; with (*c*) Zn, Cd and Hg on Au.

Here again the indication is that exact values would be very interesting. Incidentally, it is to be noted that the data plotted in Figs. 5*c*, 5*d* and the palladium and platinum values in Fig. 6*c* do not show a similar vertical relationship. It is possibly significant, however, that if the positions palladium and platinum occupy in the Periodic Table were interchanged, the results in Figs. 5*c*, 5*d* and 6*c* (but not 6*b*), would conform to the above vertical relationship.

d. Molten Solutions in Copper.

In Table IV., data are shown which have been calculated in exactly the same way, from the results obtained by Bornemann and his co-workers for molten copper alloys. The values obtained from resistivity measurements on the alloys at 1100°, 1200°, 1300° and 1400° are shown in columns 3 to 6. Column 7 shows the variation of these values between 1100° and 1400°.

The maximum and minimum values, between 1100° and 1400°, are therefore plotted (thus ●) in Fig. 6*a*, side by side with the values of the respective solid solutions. With the exception of the oxygen value (which it will be seen from Table IV. is admittedly the most variable and doubtful), these values for the molten solutions are in marked general conformity with the respective solid solution values, the former being, roughly speaking, once or twice as great as the latter.

It will be observed in Table IV. that temperature has apparently an appreciable influence on the solution resistivity of these molten alloys. The fact, however, that the atomic increases for these molten solutions are only about twice the respective solid solution values, is thought to be rather noteworthy. Moreover, it is quite possible that the solution resistivity may jump discontinuously on melting just as the resistivity of a pure metal does.

e. Solid Solutions in Magnesium and Cadmium.

Data referring to a few magnesium and cadmium solid solutions are given in Tables VI.*a* and VI.*b*, and are plotted in Figs. 6*d* and 6*e*. So far as they go they confirm the above general relationship. They also indicate,

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it is thought, a further cross-relationship between the results. The effects of silver and gold on magnesium and cadmium respectively are, for example, considerably greater than the converse effects of magnesium

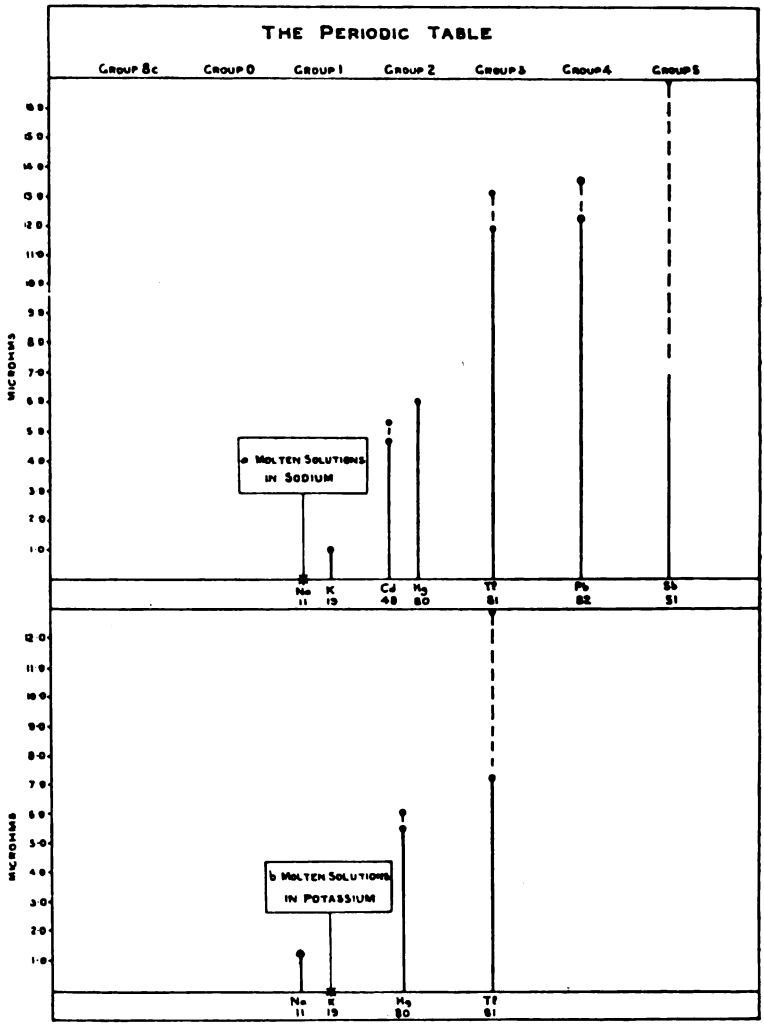

FIG. 7.—The Atomic Effects of Various Elements on the Electrical Resistivities of Sodium and Potassium. (Table VII.)

The uprights indicate: Increase in the Resistivity of the pure Solvent (in microhms per centimetre cube) due to the Presence in Molten Solution of 1·0 Atomic per cent. Added Element.)

and cadmium on silver and gold respectively. The existence of a similar type of cross relationship is also apparent in most other cases where data showing the effect of A on B, and the effect of B on A, are in both cases available.

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f. Molten Solutions in Sodium and Potassium.

In Tables VII. *a* and VII. *b* and Figures 7*a* and 7*b*, data for various molten sodium and potassium alloys—taken from papers by Bornemann, etc. (3, 4, 5), and Müller (30)—are collected and plotted. In many cases the solutions were very dilute and, therefore, the experimental difficulties of obtaining very accurate results would be considerable. They nevertheless serve to bring out the same general relationship.

Kurnakow's (25) data for solid solutions showing that rubidium has a very small atomic effect on potassium (and vice versa) are also included.

The foregoing data all refer to solutions in which the solvent has a comparatively low resistivity value. In cases where the solvent has a high resistivity value the interpretation is more difficult. In many cases, on the solute going into solution it actually lowers the resistivity of the solvent. It seems, however, that in most cases, in spite of this lowering, the solution has a higher resistivity than it would have were the components mutually indifferent—as discussed in Section 1*b*.

3. Discussion of the Results.

It is thought that the first inference to be drawn from the foregoing results is that there is—from the electrical resistivity point of view—no very obvious analogy between solid solutions and aqueous solutions.

The results indicate that the atomic resistivity effects of various elements in solid or molten solution in a metallic solvent are relatively large or small according as the solute is far from or near to the solvent in the Periodic Table. In other words, the atomic effects are large or small according as the solute differs from, or resembles the solvent, in some atomic property. It is obviously the properties of the solute in relation to those of the solvent that have to be considered.

The fact that most of the atomic properties of the elements vary periodically suggests several possible explanations.

a. Comparison with some of the Atomic Properties of the Elements.

An examination of the atomic volumes of the elements concerned shows that the above results cannot be explained as being directly due to differences of atomic volume between the solvent and the solute. For example, the differences between the following atomic volumes: Ag = 10·23, Au = 10·20, Mn = 7·44, Ni = 6·64, etc., and that of copper (Cu = 7·08) are not in the same order as the resistivity effects of these elements on copper (see Fig. 5). In the same way the data collected by Smith[1] for the intrinsic pressures of the elements (*viz.* Ni = 306,300, Fe = 239,000, Cu = 236,100, Au = 178,500, Ag = 161,900, Zn = 108,900, Al = 119,300, Sn = 68,700 megabars, etc.) are equally incapable of direct application.

Similarly with the electrical resistivities, thermo-electric properties and decomposition potentials of the elements.

As a matter of fact, the exceedingly close way in which the resistivity increases follow the relative positions of the elements in the Periodic Table, itself tends to preclude many of the atomic properties, since most of them do not follow the Periodic Table nearly so closely. The closeness of the above relationship is in fact thought to be very significant. It

[1] *Journal of the Institute of Metals*, 1917 (i), p. 78.

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suggests that the above results may be explained by assuming that the relative atomic effects are small, when there is little "affinity" between atoms of solute and solvent, and large according as the "affinity" between the two is greater. It is thought that this explanation is substantiated when the results are examined from various other points of view.

b. The Degree of Dispersion of the Solute.

It is obviously of primary importance to know the degree of dispersion of the solutes in the above cases (see Section 1*e*). It is thought that there is no experimental evidence indicating that the atoms of solute in a dilute metallic solid solution are associated. All available evidence indicates on the contrary that the solute is probably atomically dispersed. Unfortunately, however, the evidence on this point is not absolutely conclusive.

If the above results were to be explained by assuming that the atomic effects of various elements on a metallic solvent would be equal if the solutes were all dispersed to the same degree, it would be necessary to assume that the atoms of silver, gold, and zinc, for instance, in solid and molten solution in copper are associated to a highly improbable degree. In one case at all events direct comparison is possible. Cadmium is known to be atomically dispersed in boiling mercury, while resistivity data indicate that cadmium at 300° has relatively a very small atomic influence on the electrical resistivity of mercury compared, for instance, with sodium.

In what follows it will be assumed that the solutes in the dilute solid solutions quoted are in all cases atomically dispersed. It may be that in some cases there is a certain amount of association, but this does not seem probable and does not affect the general conclusions arrived at.

c. Space-Lattice Considerations.

It is thought that the foregoing explanation of the results receives support by considering the way in which the atoms of solute and solvent are arranged with respect to one another in the space-lattice.

If one atom of solute in a very dilute solid solution is pictured, and if, for example, the face-centred cube lattice is assumed, it is known from the work of W. H. and W. L. Bragg that this atom of solute will be surrounded by twelve equidistant atoms of solvent. It is thought that the solute atom will not be attached, providing the solution is sufficiently dilute, to any one of the twelve surrounding atoms in particular, although there may be strong "affinity" forces at work tending to cause such combination.

The above non-formation of inter-metallic compounds will, however, only occur in very dilute solutions. As the solutions become more concentrated some of the atoms of solute will tend to "combine with" (that is to say, a transference or re-grouping of electrons will take place) definite atoms of solvent to form inter-metallic compounds (compare Section 1*b*).

If the electrical forces between solute and solvent atoms normally tend to be more or less neutralised by inter-metallic compound formation, it seems that in the case of the dilute solid solution pictured above, these forces are not neutralised and are therefore still in existence between the solute atom and the electrons of the surrounding solvent atoms.

Incidentally, if the above picturing is correct, it follows that normal inter-metallic compounds do not exist as such in sufficiently dilute solid solutions and consequently it is correct to compare the atomic effects of various solutes on a solvent without taking into consideration the formulæ

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of the inter-metallic compounds formed by solute and solvent under more favourable conditions. If this is the case, there should be some relationship between the atomic effect of metal A on metal B and vice versa. This type of cross-relationship seems to be appearing in the results (see Section *2e*).

d. Electrical Conductivity Considerations.

The present generally accepted view on metallic conduction is that metals conduct an electric current by means of their "free" electrons. (By "free" electrons is meant such electrons as are shot off from one atom and temporarily attach themselves to a new atom.)

Temperature, it is assumed, has the effect of increasing the kinetic energy of these electrons and making them in consequence less easily deflected in the direction in which the electric current is flowing.

It seems in accordance, therefore, with the above view to explain the relatively enormous effects produced on a metallic conductor by the introduction of a few foreign atoms, by assuming that the increased resistivity is due to the solute atoms exerting forces on the electrons of the neighbouring atoms of the solvent (and vice versa) as suggested in the preceding sub-section.

To take an actual case, the fact that the addition of 1·0 atomic per cent. arsenic sends the specific resistivity of copper up by four or five microhms (this effect is apparently almost equally great near absolute zero where the resistivity of pure copper approaches 0·0) makes it seem very probable that each arsenic atom is exerting a very considerable influence on the resistivity of a large number of the surrounding copper atoms. It is thought that it would be difficult to explain such a relatively large influence unless it is assumed that the electrons in a large number of the copper atoms are being affected.

Conclusion.

Experiments are being carried out with the view of obtaining some more data of the above type. It is also hoped that a more quantitative interpretation may be possible in the future.

In conclusion, the author would like to express his appreciation of the encouragement and advice he has received from Professor C. A. Edwards, and acknowledge his indebtedness to the Commissioners for the 1851 Exhibition for a special grant made in view of a relinquished scholarship.

TABLE I.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITY OF IRON.[1]

Added element	C	N	Al	Si	P	V	Cr	Mn	Ni	Co	Cu	Mo	W	Au
Atomic weight	12·0	14·0	27·1	28·3	31·0	51·1	52·0	54·9	58·7	59·0	63·6	96·0	184·0	197·2
Increase in the resistivity of iron (in microhms per centimetre cube) due to the presence in solid solution of 1·0 atomic per cent. added element.	7·3[2]	3·6	5·8	6·9	6·1	4·6	5·0	4·9 to 5·4	1·5	1·0	4·5	5·8	4·9	3·9

[1] *Journal of the Iron and Steel Institute*, 1920 (i), pp. 640-641.
[2] Water-quenched at 1100° C., and relative to a 1·0 per cent. carbon steel.

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TABLE II.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITIES OF NICKEL, COBALT, PALLADIUM AND PLATINUM.

Author, Date and Reference.	Element.	Atomic Weight.	Increase in Resistivity (in Microhms per Centimetre Cube) due to the Presence in Solid Solution of: 1·0 Atomic Per Cent. Added Element.	Remarks.
			a. Solid Solutions in Nickel.	
Hunter and Sebast: 1917 (22)	Cr	52·0	6·5	From alloys with 5·0, 10·0, 15·0 weight per cent. chromium. Initial slope taken.
Hunter and Sebast: 1917 (22)	Mn	54·9	2·0 to 2·5	From alloys with 5·0, 8·0, 10·0, 12·5, 15·0 and 20·0 weight per cent. manganese.
Burgess and Aston: 1910 (8) Honda: 1918 (20) . .	Fe	55·9	Below 0·5 (?)	The results appear to indicate that an inter-metallic compound Fe_2Ni is formed, which is fairly soluble in iron but practically insoluble in nickel.
Ruer and Kaneko: 1913 (38).	Co	59·0	0·5 (?)	Value deduced by interpolation.
Kurnakow: 1907 (27) . .	Cu	63·6	1·0	From alloys with 10·6, 20·0, 28·0, etc., weight per cent. copper. Initial slope taken.
			b. Solid Solutions in Cobalt.	
Honda: 1919 (21) . . .	Fe	55·9	1·0 to 2·0	From alloys containing 10·0, 20·0, 30·0 weight per cent. iron. Value deduced by interpolation.
Ruer and Kaneko: 1913 (38) .	Ni	58·7	Very low	Nickel appears to form an inter-metallic compound which is practically insoluble in cobalt.

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TABLE II. (*continued*).

			c. Solid Solutions in Palladium.	
Wolf: 1914 (47) . . .	H	1·0	16·0	Calculated from Wolf's data showing the rise in resistivity of palladium wire, due to the occlusion of various volumes of hydrogen.
Geibel: 1911 14) . . .	Ag	107·9	1·4	From alloys with 9·90, 19·83, 29·77, etc., atomic per cent. silver. Initial slope taken.
Geibel: 1911 (14) . . .	Pt	195·2	0·7	From alloys with 5·7, 12·0, 19·0, 26·7, etc., atomic per cent. platinum. Initial slope taken.
Geibel: 1910 (13) . . .	Au	197·2	1·0	From alloys with 5·67, 11·9, 18·8, 26·5, etc., atomic per cent. gold. Initial slope taken.
			d. Solid Solutions in Platinum.	
Żemczużny: 1920 (24) . .	Rh	102·9	0·7 to 0·8	From alloys with 1·88, 4·63, 9·08, 17·40 atomic per cent. rhodium. Initial slope taken.
Geibel: 1911 (14) . . .	Pd	106·7	0·55 to 0·60	From alloys with 16·7, 31·5, 43·8, etc., atomic per cent. palladium. Initial slope taken.
Żemczużny: 1920 (24) . .	Pd	106·7	0·55 to 0·60	From alloys with 1·81, 4·48, 8·78 and 16·70 atomic per cent. palladium. Initial slope taken.
Geibel: 1911 (14) . . .	Ir	193·1	1·5 to 1·6	From alloys with 5·05, 10·09, 15·13, 20·16 and 25·16 atomic per cent. iridium. Initial slope taken.
Żemczużny: 1920 (24) . .	Ir	193·1	1·4 to 1·5	From alloys with 1·01, 2·53, 5·05 and 10·09 atomic per cent. iridium. Initial slope taken.

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TABLE III.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITY OF COPPER. (SOLID SOLUTIONS.)

Author, Date and Reference.	Element.	Atomic Weight.	Increase in the Resistivity of Copper (in Microhms Per Centimetre Cube) due to the Presence in Solid Solution of:		Remarks.
			a. 1·0 Per Cent. *By Weight*, Added Element.	*b.* 1·0 *Atomic* Per Cent. Added Element.	
Stepanow: 1914 (44) . .	Mg	24·3	2·0	0·8	Doubtful whether all the magnesium is in solution even in the 1·7 and 2·0 atomic per cent. magnesium alloys quoted.
Broniewski: 1912 (6) . .	Al	27·1	1·9	0·8	From alloys with 6·0 and 14·0 volume per cent. aluminium.
Hampe: 1892 (18) . .	Si	28·3	7·0	3·0	From alloys with 0·53 and 3·47 weight per cent. silicon.
Münker: 1912 (31) . .	P	31·0	(9 to 11)	(4·0 to 5·0)	Seven alloys with phosphorus from 0·0 to 1·05 per cent. by weight examined. Not solid solutions, apparently. Increased resistivity probably due to segregation of phosphide at crystal boundaries (see Edwards, Section 1*a*).
Hunter and Sebast: 1917 (22)	Cr	52·0	4·0	4·0	One alloy with 0·5 weight per cent. chromium.
Münker: 1912 (31) . .	Mn	54·9	3·4	2·9	Ten alloys with 0·04 to 1·49 weight per cent. manganese examined, only slight resistivity differences found between alloys as: (*a*) untreated, (*b*) annealed at 700°, and (*c*) quenched at 500° and 700°.
Hunter and Sebast: 1917 (22)	Mn	54·9	3·5	3·0	From alloys with 4·5, 7·3, 12·0, etc., weight per cent. manganese.
Ruer and Fick: 1913 (37) .	Fe	55·9	2·3	2·0	One alloy with 0·5 weight per cent. iron.
Reichardt: 1907 (36) . .	Co	59·0	2·5 to 3·8	2·5 to 3·5	Four alloys containing up to 3·0 per cent. by weight cobalt.

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TABLE III. (*continued*).

Kurnakow: 1907 (27) . .	Ni	58·7	1·2 to 1·3	1·1 to 1·2	Six alloys containing up to 30·0 per cent. by weight nickel. Linear increase up to about 40·0 per cent. nickel.
Gray: 1915 (15) . . .	Ni	58·7	1·2	1·1	From alloys with 10·0, 30·0 and 40·0 weight per cent. nickel.
Matthiessen: 1860 (29) . .	Zn	65·4	0·25 to 0·30	0·26 to 0·31	From alloys with 1·6 and 3·2 weight per cent. zinc.
Haas: 1894 (17) . . .	Zn	65·4	0·28	0·29	From alloys with 0·71, 1·56, 3·07, 5·51, etc., weight per cent. zinc.
Puschin: 1913 (35) . .	Zn	65·4	0·29	0·30	From alloys with 3·0, 5·0, 8·0, etc., atomic per cent. zinc.
Matthiessen: 1860 (29) . .	As	75·0	4·0 to 5·0	—	From alloys with 2·8 and 5·4 weight per cent. arsenic.
Hampe: 1892 (18) . .	As	75·0	4·5	5·3	From alloys with 0·22, 0·35, 0·81 weight per cent. arsenic.
Hiorns: 1909 (19) . . .	As	75·0	4·8	5·6	From fifteen alloys with 0·05 to 2·58 weight per cent. arsenic.
Puschin: 1913 (34) . .	As	75·0	4·7	5·5	From alloys with 0·25, 0·50, 0·75, 1·00, 1·50, etc., weight per cent. arsenic.
Matthiessen: 1860 (29) .	Ag	107·9	0·13	0·22	From alloys with 1·22 and 2·45 weight per cent. silver.
Kurnakow: 1910 (26) . .	Ag	107·9	0·08 to 0·13	0·13 to 0·22	From alloys with 0·5, 1·0, 2·0, 3·0, etc., atomic per cent. silver.
Matthiessen: 1860 (29) . .	Sn	118·7	1·4	2·6	From alloys with 1·33, 2·52 and 4·90 weight per cent. tin.
Münker: 1912 (31) . .	Sn	118·7	1·4	2·6	From ten alloys containing 0·13 to 1·46 per cent. by weight tin. Only slight resistivity differences found between alloys as: (*a*) untreated, (*b*) annealed at 700°, and (*c*) quenched at 500° and 700°.
Hampe: 1892 (18) . .	Sb	120·2	2·0 to 2·3	4·0 to 5·0	From alloys with 0·26 and 0·53 weight per cent. antimony.
Hiorns: 1909 (19) . . .	Sb	120·2	2·8 to 3·8	5·5 to 7·5	From six alloys with 0·10 to 0·61 weight per cent. antimony.
Matthiessen: 1860 (29) . .	Au	197·2	0·15 to 0·25	0·5 to 0·65	From alloys with 1·64 and 3·53 volume per cent. gold.
Kurnakow: 1916 (28) . .	Au	197·2	0·21 to 0·23	0·60 to 0·64	From alloys with 5·0, 10·0, 15·0, etc. atomic per cent. gold. Initial slope taken.

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TABLE IV.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITY OF COPPER. (MOLTEN SOLUTIONS.)

Added Element.	Atomic Weight.	Increase in the Resistivity of Molten Copper (in Microhms per Centimetre Cube) due to the Presence in Molten Solution of 1·0 Atomic Per Cent. Added Element, at :—					Remarks.
		1100°.	1200°.	1300°.	1400°.	Variation between 1100° and 1400°.	
(Resistivity of Pure Copper	—	21·52	22·41	23·29	24.17)	—	All the data given in this table are calculated from the results of: Bornemann and Rauschenplat (4) and Bornemann and Wagenmann (5).
Oxygen	16·0	0·4	0·7	1·2	1·5	0·4 to 1·5 ?	Calculated from alloy containing 0·667 atomic per cent. oxygen.
Aluminium . . .	27·1	2·0	1·9	1·8	1·8	1·8 to 2·0	Calculated from alloy containing 10·99 atomic per cent. aluminium.
Sulphur	32·1	6·3	6·3	6·4	6·5	6·3 to 7·6	Calculated from alloy with 0·43 atomic per cent. sulphur.
Sulphur	32·1	7·5	7·5	7·6	7·6	—	Calculated from alloy with 0·90 atomic per cent. sulphur.
Nickel	58·7	—	1·6	1·7	1·8	1·6 to 1·8	Calculated from alloy with 20·22 atomic per cent. nickel. (*N.B.*—In solid solutions the increase is linear up to about 40·0 atomic per cent. nickel.)
Zinc	65·4	0·6	0·7	0·8	—	0·5 to 0·8	Calculated from alloy with 0·88 atomic per cent. zinc.
Zinc	65·4	0·5	0·5	0·6	—	—	Calculated from alloy with 3·41 atomic per cent. zinc.
Silver	107·9	− 0·1	0·0	0·2	0·3	− 0·1 to 0·3	Calculated from alloy with 1·01 atomic per cent. silver.
Tin	118·7	3·7	3·8	3·9	4·0	3·7 to 4·3	Calculated from alloy with 1·08 atomic per cent. tin.
Tin	118·7	4·3	4·3	4·3	4·3	—	Calculated from alloy with 2·60 atomic per cent. tin.
Antimony . . .	120·2	8·4	8·7	8·7	8·6	8·4 to 8·6	Calculated from alloy with 1·04 atomic per cent. antimony.
Lead	207·2	4·0	4·3	4·6	5·0	3·9 to 5·0	Calculated from alloy with 0.62 atomic per cent. lead.
Lead	207·2	3·9	4·1	4·5	4·8	—	Calculated from alloy with 0·92 atomic per cent. lead.

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TABLE V.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITIES OF SILVER AND GOLD. (SOLID SOLUTIONS.)

Author, Date and Reference.	Added Element.	Atomic Weight.	Increase in Resistivity (in Microhms per Centimetre Cube) due to the Presence in Solid Solution of 1·0 Atomic Per Cent. Added Element.	Remarks.
			a. Solid Solutions in Silver.	
Smirnow: 1911 (42) . .	Mg	24·3	0·8 to 1·3	From alloys with 0·17, 0·38, 0·74, 1·03 atomic per cent. magnesium.
Broniewski: 1912 (6) . .	Al	27·1	1·6 to 2·0	From alloys with 4·9 and 9·7 volume per cent. aluminium.
Beckmann: 1914 (1) . .	Al	27·1	1·6 to 2·0	From alloys with 3·3, 4·45 and 7·6 atomic per cent, aluminium.
Matthiessen: 1860 (29) . .	Cu	63·6	0·1	From alloy with 2·01 volume per cent. copper. Doubtful if copper is all in solution.
Kurnakow: 1910 (26) . .	Cu	63·6	0·4 to 0·5	From alloys with 2·0, 4·0, 8·0 and 10·0 atomic per cent. copper.
Sedström: 1919 (41) . .	Zn	65·4	0·5	From alloys with 5·7 and 11·6 atomic per cent. zinc. Initial slope taken.
Geibel: 1911 (14) . . .	Pd	106·7	0·4	From alloys with 10·1, 20·2, 30·2, etc., atomic per cent. palladium. Initial stope taken.
Sedström: 1919 (41) . .	Cd	112·4	0·4	From alloy with 4·0 atomic per cent. cadmium.
Matthiessen: 1860 (29) . .	Sn	118·7	4·0 to 5·0	From alloys with 0·93 and 2·01 volume per cent. tin.
Matthiessen: 1860 (29) . .	Pt	195·2	0·6 to 0·7	From alloys with 5·0 and 9·8 volume per cent. platinum.
Thompson & Miller: 1906 (45)	Pt	195·2	1·0 to 1·5	From alloys with 10·5, 20·5, 31·5 weight per cent. platinum. Initial slope taken.

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TABLE V. (*continued*).

Matthiessen: 1860 (29) . .	Au	197·2	0·4 to 0·6	From alloys with 1·17, 1·74, 2·68, 5·84, etc., volume per cent. gold.
Sedström: 1919 (41) . .	Au	197·2	0·3	From alloys with 5·0, 9·7, etc., atomic per cent. gold. Initial slope taken.
			b. Solid Solutions in Gold.	
Matthiessen: 1860 (29) . .	Fe	55·9	4·0 to 6·0	From alloys with 4·7, 5·0, 10·0 and 15·0 weight per cent. iron.
Matthiessen: 1860 (29) . .	Cu	63·6	0·35 to 0·4	From alloys with 2·28, 4·33, 8·46, etc., volume per cent. copper.
Kurnakow: 1916 (28) . .	Cu	63·6	0·74	From alloys with 5·0, 10·0, 15·0 atomic per cent. copper. Initial slope taken.
Sedström: 1919 (41) . .	Zn	65·4	0·85 to 0·95	From alloys with 4·9, etc., atomic per cent. zinc. Initial slope taken.
Geibel: 1910 (13) . . .	Pd	106·7	0·3	From alloys with 17·0, 31·6, etc., atomic per cent. palladium. Initial slope taken.
Matthiessen: 1860 (29) . .	Ag	107·9	0·2 to 0·3	From alloys with 1·19, 1·77, 2·73, etc., volume per cent. silver.
Clay: 1911 (11) . . .	Ag	107·9	0·30	From alloys with 0·726, 0·872, 0·960, 1·586 and 2·550 volume per cent. silver.
Sedström: 1919 (41) . .	Ag	107·9	0·36	From alloys with 4·9, etc., atomic per cent. silver.
Saldau: 1915 (39) . . .	Cd	112·4	0·35	From alloys with 5·05, 14·4, etc., atomic per cent. cadmium.
Sedström: 1919 (41) . .	Cd	112·4	0·64	From alloys with 5·4, 8·7, etc., atomic per cent. cadmium.
Matthiessen: 1860 (29) . .	Sn	118·7	7·5 to 8·5	From alloys with 1·17 and 2·11 volume per cent. tin.
Geibel: 1911 (14) . . .	Pt	195·2	0·8	From alloys with 10·09, 20·26, 30·21, 40·25 atomic per cent. platinum. Initial slope taken.
Parravano: 1919 (33) . .	Hg	200·6	0·4	From numerous alloys containing 0·5 to 3·0 weight per cent. mercury.

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TABLE VI.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITIES OF MAGNESIUM AND CADMIUM. (SOLID SOLUTIONS.)

Author, Date and Reference.	Added Element.	Atomic Weight.	Increase in Resistivity (in Microhms Per Centimetre Cube) due to the Presence in Solid Solution of 1·0 Atomic Per Cent. Added Element.	Remarks.
			a. Solid Solutions in Magnesium.	
Broniewski: 1912 (6) . . .	Al	27·1	1·6	From alloy with 4·7 volume per cent. aluminium. Doubtful if all aluminium is in solution.
Smirnow: 1911 (42) . . .	Ag	107·9	3·0 to 3·5	From alloys with 0·44, 0·88, etc., atomic per cent. silver.
Urascow: 1911 (46) . . .	Cd	112·4	0·5 to 0·6	From alloys with 5·0, 10·0, 15·0, 20·0, etc., atomic per cent. cadmium. Initial slope taken.
Stepanow: 1914 (44) . . .	Sn	119·0	3·0	From alloys with 1·18, 2·5, 3·56, etc., atomic per cent. tin.
Stepanow: 1908 (43) . . .	Pb	206·9	4·0 to 6·0	From alloys with 0·75, 1·76, 3·03, 3·43, etc., atomic per cent. lead.
			b. Solid Solutions in Cadmium.	
Urascow: 1911 (46) . . .	Mg	24·4	0·40 to 0·45	From alloys with 5·0, 10·0, 15·0, 17·5, etc., atomic per cent. magnesium.
Saldau: 1915 (39)	Au	197·2	1·7 to 1·9	From alloy with 0·95 atomic per cent. gold.

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TABLE VII.

EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTIVITIES OF SODIUM AND POTASSIUM. (MOLTEN SOLUTIONS.)

Added Element.	Atomic Weight.	Temperature of Measurement.	Increase in Resistivity (in Microhms per Centimetre Cube) due to the Presence of 1·0 Atomic Per Cent. Added Element.	Remarks. All the Values in this Table have been Calculated from the Results of Bornemann and Rauschenplatt: 1912 (4), unless the Contrary is Stated.
			a. Molten Solutions in Sodium.	
K	39·1	100° C.	0·95 or 1·1	From alloys with 4·2 and 8·0 atomic per cent. potassium.
		150° C.	1·0 or 1·1	
		200° C.	1·1	
Cd	112·4	150° C.	5·1	From alloy with 0·93 atomic per cent. cadmium.
		250° C.	4·6	
		350° C.	5·3	
Sb	120·2	150° C.	7·0	From alloy with 0·1 atomic per cent. antimony. (In consequence of the small amount of solute there is a large possible error.)
		250° C.	11·0	
		350° C.	17·0	
Hg	200·0	100° C.	6·0	From alloys with 7·0, etc , atomic per cent. mercury.
		150° C.	5·9	
		200° C.	5·9	
Tl	204·1	150° C.	11·9	From alloy with 0·92 atomic per cent. thallium.
		250° C.	12·1	
		350° C.	13·1	
Pb	206·9	250° C.	12·3	From alloy with 0·99 atomic per cent. lead.
		300° C.	12·9	
		350° C.	13·6	
			b. Molten Solutions in Potassium.	
Na	23·0	100° C.	1·3	From alloys with 7·0, etc., atomic per cent. sodium.
		150° C.	1·3	
		200° C.	1·3	
Rb	85·5	0° and 25° C. (Solid Solutions)	0·1	Kurnakow: 1914 (25), alloys with 14·29, etc., atomic per cent rubidium.
Hg	200·0	100° C.	5·5	From alloys with 4·75, etc., atomic per cent. mercury.
		150° C.	5·8	
		200° C.	6·1	
Tl	204·1	150° C.	7·3	From alloy with 1·06 atomic per cent. thallium.
		250° C.	9·8	
		350° C.	13·2	

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LIST OF REFERENCES.

(The following references all refer to electrical resistivity data. The particular alloy systems studied in each case are shown in brackets.)

(1) Beckmann: *Internationale Zeitschrift für Metallographie*, 1914, Vol. 6, p. 246. (Ag-Al.)

(2) Benedicks: *L'Acier au Carbone*, Upsala, 1904. (Steels and General Theory.)

(3) Bornemann and Müller: *Metallurgie*, 1910, Vol. 7, p. 396. (Various Molten Alloys.)

(4) Bornemann and Rauschenplat: *Metallurgie*, 1912, Vol. 9, pp. 473, 505. (Various Molten alloys.)

(5) Bornemann and Wagenmann: *Ferrum*, 1914, Vol. 11, pp. 276, 289 and 330. (Various Molten Alloys).

(6) Broniewski: *Annales de Chimie et de Physique*, 1912, Vol. 25, pp. 5-125. (Al—Various and General Theory).

(7) Bücher: *Zeitschrift für Anorganische Chimie*, 1918, Vol. 98, p. 109. (Cd-Sn, Sn-Cd.)

(8) Burgess and Aston: *Metallurgical and Chemical Engineering*, 1910, Vol. 8. (Ni-Fe, Fe-Ni.)

(9) Campbell: *Journal of the Iron and Steel Institute*, 1916, (ii), p. 287. (Tempering of C steels.)

(10) Campbell: *Journal of the Iron and Steel Institute*, 1918, (ii), p. 421. (Tempering of C steels.)

(11) Clay: *Jahrbuch der Radioaktivität*, 1911, Vol. 8, p. 383. (Au-Ag.)

(12) Edwards: *The Physico-Chemical Properties of Steel* (2nd edition), p. 264. (General Theory.)

(13) Geibel: *Zeitschrift für Anorganische Chemie*, 1910, Vol. 69, p. 38. (Au-Pd, Pd-Au.)

(14) Geibel: *Zeitschrift für Anorganische Chemie*, 1911, Vol. 70, p. 241. (Pd-Ag, Ag-Pd, Au-Pt, Pt-Ir, Pd-Pt, Pt-Pd.)

(15) Gray: *Ferrum*, 1915, Vol. 13, p. 85 (Abstract). (Cu-Ni.)

(16) Guertler: *Journal of the Institute of Metals*, 1911, No. 2, Vol. 6, p. 135. (General Theory.)

(17) Haas: *Wiedemann's Annalen der Physik*, 1894, Vol. 52, p. 673. (Cu-Zn.)

(18) Hampe: *Chemiker Zeitung*, 1892, Vol. 16, p. 726. (Cu-Si, Cu-As, Cu-Sb.)

(19) Hiorns and Lamb: *Journal of the Society of Chemical Industry*, 1909, p. 451. (Cu-As, Cu-Sb.)

(20) Honda: *Tokio Science Reports*, 1918, Vol. 7, p. 59. (Ni-Fe and Fe-Ni.)

(21) Honda: *Tokio Science Reports*, April, 1919. (Fe-Co, Co-Fe.)

(22) Hunter and Sebast: *Journal of the American Institute of Metals*, 1917, Vol. 11, p. 115. (Ni-Cr, Ni-Mn, Cu-Cr, Cu-Mn.)

(23) Irmann: *Metall and Erz*, 1916, Vol. 12, p. 358. (Ni-W.)

(24) Żemczużny: *Revue de Métallurgie*, 1920, p. 142 (Abstract). (Pt-Rh, Pt-Pd, Pt-Ir.)

(25) Kurnakow and Nikitinsky: *Zeitschrift für Anorganische Chemie*, 1914, Vol. 88, p. 155. (K-Rb, Rb-K.)

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(26) Kurnakow, Puschin and Senkowsky: *Zeitschrift für Anorganische Chemie*, 1910, vol. 68, p. 132. (Cu-Ag, Ag-Cu.)
(27) Kurnakow and Żemczużny: *Zeitschrift für Anorganische Chemie*, 1907, Vol. 54, p. 159. (Cu-Ni, Ni-Cu.)
(28) Kurnakow, Żemczużny and Zasedatelev: *Journal of the Institute of Metals*, 1916, No. 1, Vol. 15, pp. 315-324. (Au-Cu, Cu-Au.)
(29) Matthiessen: *Poggendorf's Annalen*, 1860, Vol. 110. (Various Alloys.)
(30) Müller: *Metallurgie*, 1910, Vol. 7, pp. 730 and 755. (Various Molten Alloys.)
(31) Münker: *Metallurgie*, 1912, Vol. 9, Figs. 189-192. (Cu-P, Cu-Mn, Cu-Sn.)
(32) Norbury: *Journal of the Iron and Steel Institute*, 1920, (i), Vol. 101, p. 627. (Fe—Various.)
(33) Parravano and Jovanovich: *Gazetta Chimica Italiana*, 1919, Vol. 49, p. 1. (Au-Hg, Ag-Hg.)
(34) Puschin and Dischler: *Zeitschrift für Anorganische Chemie*, 1913, Vol. 80, pp. 65-70. (Cu-As.)
(35) Puschin and Rjaschsky: *Zeitschrift für Anorganische Chemie*, 1913, Vol. 82, p. 53. (Cu-Zn.)
(36) Reichardt: *Drudes Annalen*, 1901, Vol. 6, p. 842. (Cu-Co.)
(37) Ruer and Fick: *Ferrum*, 1913, Vol. 11, p. 48. (Cu-Fe, Fe-Cu.)
(38) Ruer and Kaneko: *Ferrum*, 1913, Vol. 10, p. 258. (Ni-Co and Co-Ni.)
(39) Saldau: *Internationale Zeitschrift für Metallographie*, 1915, Vol. 7, p. 3. (Cd-Au, Au-Cd.)
(40) Schleicher: *Zeitschrift für Elektrochemie*, 1912, Vol. 18, p. 998. (Cu-Hg.)
(41) Sedström: *Annalen der Physik*, 1919, Vol. 59, iv, p. 134. (Various Cu, Ag and Au alloys.)
(42) Smirnow and Kurnakow: *Zeitschrift für Anorganische Chemie*, 1911, Vol. 72, p. 45. (Mg-Ag, Ag-Mg.)
(43) Stepanow: *Zeitschrift für Anorganische Chemie*, 1908, Vol. 60, p. 209. (Pb-Mg, Mg-Pb.)
(44) Stepanow: *Internationale Zeitschrift für Metallographie*, 1914, Vol. 6, p. 256 (Abstract). (Mg-Sn, Mg-Zn, Mg-Cu, Mg-Bi.)
(45) Thompson and Miller: *Journal of the American Chemical Society*, 1906, Vol 28 (ii), p. 1115. (Ag-Pt.)
(46) Urascow: *Zeitschrift für Anorganische Chemie*, 1911, Vol. 73, p. 39. (Mg-Cd, Cd-Mg.)
(47) Wolf: *Zeitschrift für Physikalische Chemie*, 1914, Vol. 87, p. 575. (Pd-H.)

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DISCUSSION.

Professor T. M. Lowry said he would like to say a word in appreciation of this paper. He had been teaching physical chemistry for twenty years and during the greater part of that time he had been trying to extract physico-chemical information from metallurgists; he knew of no group of people who had so much knowledge hidden away, and it was very hard to get it. Mr. Norbury's paper gave him just the kind of information he was seeking. One thing which appealed to him strongly in the paper was that there seemed to be some sort of parallellism between electrical resistance and hardness, and he thought there were distinct indications that the two properties ran together.

Professor A. W. Porter asked if the author had considered the view put forward by the late Lord Rayleigh that increased resistance was due to a thermo-electric effect or E.M.F., set up between the atoms or molecules of which the alloys were constituted.

Dr. H. Borns: I quite agree with Dr. Lowry. It is a great pity that this valuable paper should come on at so late an hour. Two remarks occur to me. With respect to Schleicher's experiments on the resistance of conductors made up of copper wire and mercury, I do not think that Mr. Norbury quite restates Schleicher's conditions. I had a hurried look at the original paper (*Zeitschrift für Elektrochemie*, 1912, p. 998) just before the meeting; the point would require a detailed quotation. As regards the jump in the resistivity of pure metals at their melting points (see 2 (*d*) in the paper) I might mention that Pélabon in his recent experiments on the thermo-electric power of metals does not refer to any discontinuity; he does not appear to have paid particular attention to the melting point, however. Professor Porter did some work in this field some years ago, I think.

Professor Porter said that experiments had been made by Mr. Vanstone in his laboratory. There is certainly a discontinuity on melting in the case of pure metals. During his own work (in conjunction with Mr. F. Simeon) on the amount of change in the conductivity of mercury and sodium at melting point, there was a very distinct drop at the melting point. There was an interesting paper in the *Phil. Mag.* for Nov. 1920, in which similar experiments on thermal conductivity had been done on a very large number of substances. His own experiments showed that the abrupt change was the same for both kinds of conductivity in the case of the pure metals experimented.

Dr. J. L. Haughton wrote that he had read Mr. Norbury's paper with great interest, and much regretted being unable to be present at the discussion. There were one or two points which he would like to raise.

In the first place he wished to say that he considered the results shown in Figs. 5, 6 and 7 to be exceedingly important, and that it would be well worth repeating the experiments under better conditions. The author

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evidently realises that the experimental results are not all that are to be desired, for he states that "the present interpretation of the subject is essentially of a qualitative nature". One of the refinements which is necessary if quantitative results are to be obtained, is so to treat the specimens as to ensure that they are in equilibrium. That this has not been done in some cases at any rate, is obvious from the statement in paragraph *c*, that cored structures were observed under the microscope.

The figures for the resistivity of worked and of annealed metal are interesting. It would not be expected that there would be much difference between the resistivities, on the assumption that work hardness is due to the formation of amorphous material. The amorphous material is merely an under-cooled liquid, and it appears to be a general rule that temperature has little effect on the resistivity of liquid metals, so that it may be safely assumed that the resistance of the amorphous material is the same (or at any rate not greater) than that of the liquid. Roughly speaking the liquid resistivity of metals is five times that of solid metals so that a worked pure metal may be regarded as a duplex material consisting of aggregates—in large quantity—of a material having a resistivity ρ, together with a very small quantity of a material having a resistivity 5ρ. In the drawn wire referred to in the paper the tendency would be for these materials to be more or less in parallel, and thus according to Schleicher's results, the conductivity should approach to being a linear function of the composition, but even assuming the extreme case that the resistivity of the mixture was a linear function of the composition, the volumes of amorphous material present, to give the figures referred to by the author, would be approximately 4 per cent., 2 per cent., and 1 per cent. for silver, copper, and gold respectively, using the rough data referred to above.

An amount of this order would probably satisfy most of the demands made on the amorphous theory.

With regard to grain size in pure metals, it would be expected that the effect would be exceedingly small as the amount of amorphous metal at the crystal boundaries is almost certain to be very small.

Mr. Norbury replying to the discussion said, in answer to Professor Lowry, that Kurnakow and other Russian investigators had shown there was a decided similarity between the electrical resistivity curves and the hardness curves in certain binary alloy systems. As Professor Lowry pointed out, the results in the paper also indicated that the two properties ran together. For instance, referring to Fig. 6*a*, manganese and tin had much larger atomic effects than aluminium and zinc on the resistivity of copper, and in a similar way the former pair of elements had much larger hardening effects on copper than the latter pair. He did not, however, think that the relationship between the two properties was an absolutely direct one, it seemed as if probably the atomic volume of the solute had also to be taken into account.

Lord Rayleigh's theory, mentioned by Professor Porter, had he believed been rather modified, more especially in view of some work done by Dr. R. S. Willows (*Phil. Mag.*, 1907 (vi) **12**, p. 604), who examined the resistance of alloys to alternating currents, but could detect no "false resistance" due to thermo-electric forces. Nernst, for instance (*Theor. Chem.*, 1911, p. 409), suggests it is better to assume "that when an electron passes from the sphere of influence of one molecule into that of another kind of molecule, its velocity is increased on entering and decreased on leaving".

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With regard to Dr. Borns' point concerning the summary of Schleicher's work, that was an abstract from the *Journal of the Institute of Metals.* The two curves in Fig. 1 were only theoretical and were not Schleicher's actual curves. The point with respect to the jump in the resistivity of metals on melting had very appropriately been answered by Professor Porter.

Mr. Norbury in reply to Dr. Haughton wrote that he thanked him for his communication and being very much interested by the application of the amorphous theory, wished to submit some more definite data bearing on the subject.

Alkins (*Journ. Inst. Metals*, 1920 (i), p. 440), gives figures indicating that a hard drawn copper wire, obtained by heavily drafting a 0·56 inch unannealed bolt down to 0·05 inch, would only have a resistivity about 3 per cent. higher than when in the completely annealed state. The percentage of amorphous material present in such a hard drawn wire—which had been heavily drafted and had undergone a 99 per cent. reduction in area—was at present an unsettled problem. He thought, however, that Alkins' other results indicated that the percentage would be high in the case quoted, no matter how one defined the exact nature of the amorphous material formed on cold-working. If the percentage was high in such a case, he thought one would have to assume that the amorphous material in copper had a very much lower resistivity than the molten metal, whose resistivity at 1100° was 21·5 microhms.

Communication received from **Professor E. D. Campbell,** University of Michigan, March 2, 1921.

During the ten years or so following the enunciation, in 1887, of the electrolytic dissociation theory of solutions, an enormous amount of experimental work intended to test the validity of this theory, was carried on in chemical laboratories throughout the world. While in most of this work the concentrations of the solutions used were expressed in terms of gram molecules of solutes per litre, or fractions thereof, a certain number of physical chemists, particularly some of those in France, published results of carefully conducted experiments in which the concentrations of the solutions were expressed in terms of molecules of solute to one hundred molecules of solvent. This system of expressing concentrations of solutions in terms of molecule per cent. of solute to solvent was found by experience to have so many disadvantages that the usual system of expressing compositions of liquid solutions in terms of molecular concentration in unit volume has become practically universal. In 1898 Le Chatelier published his now classical researches on the influence of chemical composition on the electrical resistance of steel. He clearly recognised the close analogy between, if not the unity of mechanism, of metallic and aqueous solutions, when he expressed the composition of his metallic solutions in terms of atom per cents.

In his very interesting paper Mr. Norbury has presented in excellently arranged tables a large amount of valuable data showing the influence of various solutes on the electrical resistance of a number of metallic solvents. The results of changes in specific resistance, like those of Le Chatelier, are expressed in microhms per cm.^{3}, while the concentrations bringing about this effect are expressed in atom per cents., that is, one atom of solute to one hundred atoms of alloy.

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TABLE I.

THE EFFECT OF VARIOUS ELEMENTS ON THE ELECTRICAL RESISTANCE OF TWO OR MORE SOLVENTS.

Composition.		Computed Density.	Milligram atom per cm.^{3}	Change in michroms per cm.^{3} due to	
Solute 1 atom %.	Solvent 99 atoms %.			1·0 atom %.	1·0 milligram atom per cm.^{3}
Al	Fe	7·8	1·41	5·8	4·1
,,	Mg	1·75	·72	1·6	2·2
,,	Ag	10·4	·97	1·6 to 2·0	1·7 to 2·1
,,	Cu	8·9	1·41	·8	·6
Fe	Au	19·0	·97	4·0 to 6·0	4·1 to 6·1
,,	Cu	8·9	1·40	2·0	1·4
,,	Co	8·7	1·47	1·0 to 2·0	·7 to 1·4
,,	Ni	8·9	1·52	·5 ?	·3 ?
Cu	Fe	7·8	1·40	4·5	3·2
,,	Ni	8·9	1·51	1·0	·7
,,	Au	19·0	·97	·35 to ·74	·36 to ·76
,,	Ag	10·5	·98	·1 to ·5	·1 to ·5
Ag	Mg	1·85	·73	3·0 to 3·5	4·1 to 4·8
,,	Pd	12·1	1·13	1·4	1·2
,,	Au	19·1	·97	·2 to ·4	·2 to ·4
,,	Cu	8·9	1·39	·08 to ·13	·06 to 09
Sn	Au	19·1	·97	7·5 to 8·5	7·7 to 8·8
,,	Ag	10·5	·98	4·0 to 5·0	4·1 to 5·1
,,	Mg	1·80	·71	3·0	4·2
,,	Cu	8·9	1·39	1·4	1·0
Au	Fe	7·9	1·37	3·9	2·8
,,	Pd	12·2	1·13	1·0	·9
,,	Ag	10·6	·98	·3 to ·6	·3 to ·6
,,	Cu	8·9	1·38	·15 to ·25	·11 to ·18
Cr	Ni	8·9	1·52	6·5	4·3
,,	Fe	7·8	1·41	5·0	3·6
,,	Cu	8·9	1·40	4·0	2·8
Mn	Fe	7·8	1·40	4·9 to 5·4	3·5 to 3·8
,,	Cu	8·9	1·40	2·9 to 3·0	2·1 to 2·2
,,	Ni	8·9	1·52	2·0 to 2·5	1·3 to 1·6
Ni	Cu	8·9	1·40	1·2 to 1·3	·9
,,	Fe	7·8	1·40	1·5	·8
,,	Co			very low	very low
Co	Cu	8·9	1·40	2·5 to 3·5	1·8 to 2·5
,,	Fe	7·8	1·40	1·0	·7
,,	Ni	8·9	1·52	·5 ?	·3 ?
Zn	Au	19·0	·97	·85 to ·95	·88 to ·98
,,	Ag	10·5	·98	·5	·5
,,	Cu	8·9	1·40	·25 to ·30	·18 to ·22
Cd	Mg	1·80	·72	·5 to ·6	·7 to ·8
,,	Au	19·0	·97	·35 to ·64	·36 to ·66
,,	Ag	10·5	·98	·4	·4
Pt	Ag	10·6	·98	·6 to 1·5	·6 to 1·5
,,	Au	19·3	·97	·8	·8
,,	Pd	12·2	1·13	·7	·6
Mg	Ag	10·4	·97	·8 to 1·3	·8 to 1·3
,,	Cu	8·9	1·41	·8	·6
Si	Fe	7·8	1·41	6·9	4·9
,,	Cu	8·9	1·41	3·0	2·1
P	Fe	7·8	1·41	6·1	4·3
,,	Cu	8·9	1·41	4·0 to 5·0	·53 to ·58
Pd	Pt	21·5	1·04	·55 to ·60	2·8 to 3·5
,,	Au	19·1	·97	·3	·3

The specific resistance of all pure metals and of metallic solutions is expressed in terms of microhms per cm.^{3} Since the changes in specific

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resistance due to solutes in solution are expressed in microhms per cm.^{3}, it would seem more logical to express the changes in concentrations of the solutes in terms of atomic concentration per cm.^{3}, rather than in atom per cents. This latter take no cognisance of the weight of solute or solvent contained in one cubic centimeter, although this is the unit to which the electrical resistances are reduced.

The desirability of completely recognising the essential unity of mechanism of metallic and aqueous solutions was brought to the attention of the Faraday Society in a paper entitled "The Solution Theory of Steel and the Influence of Changes in Carbide Concentration on the Electrical Resistance" (*Trans. Far. Soc.*, Vol. XV., Part 3, June, 1919) of which the atomic concentration in milligram atoms per cubic centimeter could be easily computed from data giving analysis in weight per cent. and the specific gravity. If the complete analysis of an alloy is known in weight per cent., the total atomic concentration can be readily found, so that if desired the number of atoms of any element present per one hundred of alloy may be easily computed.

In order to study the influence on the electrical resistance of one milligram atom per cm.^{3} of the various solutes and solvents given in the paper under discussion, most of the values for solid solutions have been computed into milligram atoms per cm.^{3}, from which the influence of one "millatom" is easily found. The arrangement of data has been changed in order to bring out a little more clearly the influence of each solute on all the solvents on which values are reported. In Table I. are given those values in which either four, three or two solvents were used with each solute. Under each of these groups the solutes are arranged in order of atomic weight and with each solute the solvents are arranged in order of the amount of effect due to each added "millatom" per cm.^{3}

In Table II. are given the values obtained with eleven solutes not given in Table I., but only one solvent with each solute.

TABLE II.

THE EFFECT OF DIFFERENT ELEMENTS ON THE ELECTRICAL RESISTANCE OF DIFFERENT METALS.

Composition.		Computed Density.	Milligram atoms per cm^3	Change in microhms per cm^3 due to	
Solute 1 atom %.	Solvent 99 atoms %.			1·0 atom %.	1·0 milligram atom per cm^3.
H	Pd	12·1	1·15	16·0	13·9
C	Fe	7·8	1·42	7·3	5·1
V	Fe	7·8	1·41	4·6	3·3
As	Cu	8·9	1·40	4·0 to 5·0	2·8 to 3·5
Mo	Fe	7·9	1·40	5·8	4·1
Rh	Pt	21·5	1·04	·7 to ·8	·7 to ·8
Sb	Cu	8·9	1·39	2·0 „ 3·8	1·4 to 2·7
W	Fe	8·0	1·37	4·9	3·5
Ir	Pt	21·5	1·01	1·4 to 1·6	1·4 to 1·6
Hg	Au	19·1	·97	·4	·4
Pb	Mg	1·8	·70	4·0 to 6·0	5·7 to 8·6

A study of the data given in Tables I. and II. clearly indicates that Mg and Fe seem to have not less than twice the dissociating—or if the

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expression is preferred—dispersing power of any of the other metals on which three or more values are recorded. This is best shown by means of Table III., in which the first column gives the solvent, the second column the number of cases reported, and the third column the mean effect on specific resistance of all the values reported for one milligram atom per cm.[3]

TABLE III.

I.	II.	III.
Mg	5	3·75
Fe	13	3·4
Au	9	1·9
Cu	15	1·5
Ni	5	1·4
Ag	9	1·2
Pd	3	·9
Pt	3	·9

Mr. Norbury, in reply, wrote that Professor Campbell in his numerous papers, which had done so much to develop the subject, had drawn analogies between aqueous solutions and metallic solid solutions, and in his present communication he again insisted on their essential unity of mechanism. Although the two types of solution were probably very similar if the nature of the forces holding the solute in solution was being considered, he thought the way in which they reacted when conducting an electric current was vitally different in the two cases. The generalisation brought out in the paper indicating the relative atomic effects of various solutes on a metallic solvent, was very different from that obtaining in aqueous solutions.

Professor Campbell pointed out that if one wished to compare the atomic resistivity increases in one solvent with those in another solvent, one had to take into account the fact that "centimetre cubes" of different solvents did not contain equal numbers of atoms. For comparisons of this type he had been reducing the results to "atomic resistivities" (*i.e.*, specific resistivity ÷ $\sqrt[3]{\text{atomic volume}}$).

He did not think it was permissible to deduce values showing the average atomic effects of various solutes on a metallic solvent as had been done in column 3 of Professor Campbell's Table III. Taking, for instance, the extreme cases of the values so obtained for Pd and Pt, it would be seen from Fig. 5 that the few results available in these cases all referred to solutes which were close to the solvent in the Periodic Table. The "average" value deduced from such solutes was consequently relatively low and not comparable with an "average" value similarly deduced from the more general copper data in Fig. 6*a*.

An attempt had, as a matter of fact, been made, by working along the lines indicated in Sections 2*e* and 3*c* of the paper, to see if constants, typical of each metal acting as a metallic solvent, existed. By doing so the following relative values were estimated :—

Ag = 9, Cu = 10, Au = 12, Al = 13, Cd = 17,
Fe = 18, Ni = 20, Mg = 22, Pt = 25, Pd = 30.

Further data were, however, being obtained with the view of investigating this particular cross-relationship.

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REVIEWS OF BOOKS.

Dictionary of Applied Chemistry. Edited by SIR EDWARD THORPE, C.B. LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. I., A—Calcium. Pp. 752. (London, 1921: Longmans, Green & Co. Price 60s. net per Vol.).

Thorpe's Dictionary occupies a unique position among English technical reference books, and the many chemists who are constantly making use of it will extend a hearty welcome to the new edition, since the need for a revision of this important work has for some time been apparent. It is anticipated that the new edition will run into seven volumes though possibly six will suffice. For this reason many of those who have a copy of the edition now being superseded would have preferred that the new information should have been presented in a supplementary volume as in this case they would have been put to very much less expense.

In a work of this kind several points are of supreme importance. Firstly, each contributor should be a recognised authority on the subject with which his article deals, and not merely an eminent chemist. Unfortunately this has not been secured in the case of many of the articles though it would be invidious to specify particular instances. Further, the information should be reliable, but that this is not always so will be evident from a few examples which follow. They were encountered during a brief examination of one or two articles. On page 31, under Acetoacetic Acid, we read "Arnold makes use of a colour reaction with acetophenone". No details are given as to the manner in which the test is to be applied so the original literature must be consulted, and it is then found that the reagent is not acetophenone, but the diazotised para-amino derivative of that substance. However, it is not always so easy to make use of a reference, for, on page 143, column 2, line 15, we find a reference to the work of Hunter, supposedly in the *Biochem. J.*, an English periodical. Anyone who has actually consulted the paper will remember that it appeared in the *J. Biol. Chem.* which is published in America. These examples would seem to indicate that the reader should hold suspect anything he reads in the volume unless he can be sure that it is correct from his own knowledge, or until he has confirmed it by consulting another authority, but the excellence of many of the articles and the care with which they have so evidently been written leads one to hope that such instances are isolated.

A third desideratum is that each article should be up-to-date. Among the many omissions which might be cited are the lack of any reference to the new indicators now so extensively employed, such as naphtholphthalein, thymolphthalein, phenolsulphonephthalein, and the bromcresol derivatives (Acidimetry), to "cupferron" (Analysis), to acetaldehyde obtained as a by-product in the modified yeast fermentation in which glycerol is the main product (Acetaldehyde), to alcohol obtained from the ethylene present in coke-oven gas (Alcohol), and to Claude's improved Haber process for the manufacture of ammonia (Ammonia).

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In fact the information withheld is often as valuable as the information given in the articles. As an example of a case in which the latest information has not been included we may take the description on page 76 of adenine-uracil-dinucleotide. Recent research has shown that the compound so described does not exist and that the substance isolated was a mixture.

The usefulness of the work would have been increased ten-fold by the inclusion of an exhaustive index to each volume such as is found in Ullmann's *Enzyklopädie der technischen Chemie* of which the first eight volumes have now been published. Taking such a well-known substance as aluminium chloride one is referred to no less than thirty pages in these volumes and on turning up the pages indicated in the several indexes one sees that mention of its use is made in such articles as those on Benzaldehyd, Benzolabkömmlinge, Carbonisation, Cellulose, Chlorieren, Druckerei, Durol, Erdöl, Färberei, and Katalyse, in addition to the main entry under Aluminiumchlorid.

These criticisms are intentionally somewhat severe, but it is hoped that they will be of some use both as regards the forthcoming volumes of this edition as well as for further editions which will certainly be called for. Many new articles have been written for the present edition and a large number of the existing articles have been revised and amplified. Several of the more important articles included in this first volume have already been mentioned. Among the remainder are Acetic Acid, Acetylene, Alizarin and Allied Colouring Matters, Arsenic, Assaying, Azo Colouring Matters, Balance, with an addendum "On Highly Refined Weighing," Barium, Brewing, and Calcium.

British chemists are indebted beyond measure to Sir Edward Thorpe for his zeal in again undertaking the formidable task of supervising the revision of a work so essential to all who have any share in developing the chemical industry of this country.

A System of Physical Chemistry. By WILLIAM C. McC. LEWIS, M.A., D.Sc., (Liv.), Brunner Professor of Physical Chemistry in the University of Liverpool. (Text-Books of Physical Chemistry, edited by SIR WILLIAM RAMSAY and F. G. DONNAN.) In three volumes. Vol. II. Thermodynamics. Third Edition. (London, 1920: Longmans, Green & Co. Pp. 454. Price 15s. net.)

The third edition of Professor Lewis' well-known "System of Physical Chemistry," the second edition of which we reviewed at some length in our Vol. XV., Part 1, of December, 1919, is so far limited to the second volume on Thermodynamics, and the changes made consist of additions and a few corrections. We also notice one omission, the section on the false or apparent equilibria of Duhem. Most of the additions concern problems which have formed the subjects of recent discussions before the Faraday Society, particularly on ionisation and colloids, and special reference is made to recent American work on ionisation. A résumé is given of the experimental evidence in support of Donnan's theory of membrane equilibria and of the concept of micelle in electrolytic colloids; in this section one misses reference to Nägeli and Zsigmondy. The additions do not all deal with quite recent researches, however. Thus the experiment of Des Coudres (1893) and of Tolman (1910) on gravitation and centrifugal voltaic cells are described. We mention also the description of the modified apparatus which Cottrell designed in 1919 for the determination of boiling points; the Beckmann thermometer bulb is suspended a little above the liquid within a narrow glass tube in which it remains coated with a thin film

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of the boiling liquid. Washburn and Read found this method useful for studying the boiling-point law.

The Principles of the Phase Theory. Heterogeneous Equilibria between Salts and their Aqueous Solutions. By DOUGLAS A. CLIBBENS, PH.D., Lecturer in Inorganic and Physical Chemistry in the University of London, King's College. (London, 1920: Macmillan & Co., Ltd. Pp. xx + 383, with 198 figures. Price 25s. net.)

Most of the literature on the Phase Rule that has been published in England has dealt broadly with general principles and with typical cases selected as illustrations. The systematic collection of data has been undertaken more frequently abroad, although in the special field of metallic alloys a systematic and comprehensive bibliography has been given by Professor Desch as an appendix to his "Metallography". Dr. Clibbens' book is noteworthy for the large collection of data which it presents in reference to the special case in which water is one of the components of the system. The industrial importance of the detailed study of the equilibrium between salts and water is now generally realised, especially as applied to cases of double-decomposition, where it is desired to secure from a balanced action the largest possible yield of one member of a reciprocal salt pair; moreover the scientific interest attaching to these equilibria is increased rather than diminished as one case after another is made the basis of investigation and added to the list of those on which precise information is available.

The book is divided into five long chapters, and illustrated by nearly 200 diagrams, including 28 folded sheets on which the illustrations can be seen at the same time as the text. Although too substantial to be easily read as a text-book even by the more advanced classes of students, the book will be found indispensable as a work of reference by all those who are concerned with the crystallisation of salts from solution either on the scientific or on the industrial side.

The Physical Chemistry of the Metals. By RUDOLF SCHENCK. Translated by REGINALD S. DEAN. (New York and London, 1919: John Wiley & Sons. Pp. 231. Price 17s. 6d.)

Dr. Schenck's work, which appeared in 1909, is well known to metallurgists as a convenient summary of the applications of physical chemistry to the problems of metallurgy, and it is perhaps better suited than any other to serve as an introduction to the scientific treatment of smelting reactions and metallurgical processes generally. It also includes a brief, but suggestive outline of the principles of metallography, although it makes no pretence to be a text-book of that study. Since its first publication, however, several of the problems of equilibrium with which it deals have been re-investigated and the quantitative relations in smelting and similar processes have been established with greater precision. It would therefore have been well to subject the work to a thorough revision before presenting it to readers who are unfamiliar with the German edition. There is no doubt that such a work serves a most useful purpose, and that its study may lead many chemists, who are more or less familiar with some of the technical processes of metal-smelting, to examine them in the light of our modern knowledge of equilibria in reacting systems, especially those in which both gases and solids are involved. The future advance of the metallurgical industries depends

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on the systematic study of such physico-chemical conditions, which determine the yields and efficiencies of the processes employed. The presentation of Schenck's work in an English form is therefore fully justified. The revision is limited, however, to the substitution of later values of some of the numerical data in the earlier chapters, and the addition of some footnotes. One new section has been added, on the electron theory of passivity, which, in view of the express exclusion of electro-chemistry from the scope of the treatise, appears a little arbitrary. The translation is usually smooth and readable, but contains rather numerous inaccuracies, and mis-spellings of proper names, for which the original author is in no way responsible, abound. The printing is good, and the illustrations are well reproduced.

The Physico-Chemical Properties of Steel. By PROFESSOR C. A. EDWARDS. Second Edition. (London, 1920: Charles Griffin & Co., Ltd. Pp. 281. Price 21s. net.)

This is a revised edition of Professor Edward's work on the constitution of the stee'.s. It retains the general arrangement of the first edition, but has undergone revision throughout, so as to incorporate the most important investigations in this branch of metallurgy during the last four years. Since the author has himself been actively engaged in this work of investigation, he is able to write with first-hand knowledge of his subject, and the revision naturally exhibits his own attitude on many controversial points. This is as it should be, and Professor Edwards states his case clearly and fairly. This is particularly noticeable in the chapter on the hardening of steel, in which the view is maintained that the hardness of quenched steel and aluminium bronze is due to the presence of amorphous material, formed along planes of twinning. As is well known, the author, in collaboration with Professor Carpenter, has made important contributions to our knowledge of twinning in metals, so that his opinion deserves consideration, even if it may not command acceptance. The chapter on the determination of hardness has been revised to include an account of impact methods of measuring this property, and a discussion of hardness as an atomic property. This is a subject of perennial interest, and we are still far from being able to determine any precise relation between hardness, as understood in the workshop, and any of the more fundamental physical properties.

A large part of the book is devoted to alloy or special steels, and this section is somewhat less satisfactory. A large mass of data is presented, largely in the form of extracts from original papers, but a comprehensive survey of the subject is lacking. It is true that in the present changing state of our knowledge of these steels, such a survey would be no easy task but the effort would be one well worth making. It is rather surprising that the nickel-chromium steels, among the most important of all those employed by the modern engineer, are scarcely discussed, although the author has repeatedly shown an interest in their study. An account of recent work on the electrical conductivity of steels, and its relation to their constitution, concludes a very useful book.

The Chemical Analysis of Steel Works Materials. By FRED IBBOTSON, B.Sc.I, F.R.C.Sc., F.I.C. (London, 1920: Longmans, Green & Co. Pp. 296. Price 21s. net.)

This book is a new edition of that section of Brearley and Ibbotson's "The Analysis of Steel Works Materials," published in 1902, which dealt with the analytical chemistry of the raw materials and finished products of ferrous metal-

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lurgy. As the author states in his preface, this new edition has long been overdue, but on this account it will probably be all the more welcome to those whom the subject interests.

The older work was one which no analyst engaged in a steel works could afford to be without, and although some very useful sections in the older book have been left out in the new, the same remark still holds good in respect to this edition. A comparison of the methods described in the two editions gives a very good index of the considerable changes which have taken place during the last eighteen years.

The author is to be congratulated on the excellence of the arrangement adopted and on the clear and concise manner in which the book is written. His plan is first to describe the principle of the various methods which have been proposed from time to time for the estimation of an element, and then to give in detail those which are in general use at present. This arrangement to a large extent compensates for the omission of the excellent Bibliography which formed a part of the earlier edition.

There is generally very little that calls for criticism in the methods as described in the book. We do not, however, agree with the author's statement on page 123 that dimethyl glyoxime is suitable for separation of mixtures of cobalt and nickel in any proportion. We find that small quantities of nickel are not effectively separated from large quantities of cobalt by this reagent.

Rapid Methods for the Chemical Analysis of Special Steels, Steel-making Alloys, their Ores and Graphites. By C. M. JOHNSON, PH.M. Third Edition. (New York, 1920: John Wiley & Sons, Inc. Pp. xi + 552. London: Chapman & Hall, Ltd. Pp. 552. Price 36s. net.)

This book has all the characteristic features of the former editions, and also over 100 pages of new matter, including the determination of zirconium, cerium, tantalum, and a new method for uranium. The book will be very useful, as it contains provision for almost any complexity of modern ferrous alloys and the way in which one element interferes with the determination of another, it will be seen that Mr. Johnson's is no mean achievement.

An original feature is the frequent use made by the author of reactions neglected by other chemists. There is no doubt, however, that there is too much detail specified. As it stands, the book makes precisely the same demand on the intelligence of the user as a cookery book. A trained chemist will frequently be able to cut across the tortuous paths that the author prescribes, as some of the methods are by no means rapid.

A Metallographic Study on Tungsten Steels. By AXEL HULTGREN. (New York: John Wiley & Sons. London, 1920: Chapman & Hall, Ltd. Pp. 95, and also 76 reproductions of photomicrographs. Price 16s. 6d. net.)

The author has limited himself to ternary alloys of carbon, tungsten, and iron, and has studied :—

(1) The transformations during different heat treatments and the structures thereby formed.

(2) Carbides in tungsten steels.

He first reviews previously published work without comment, and then gives his own experiments and conclusions. These are followed by a criticism of the results of previous investigators, and finally a summary of the whole study is given.

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There is a long appendix containing a discussion of the work of Honda and Murakami. The experimental methods used are the heating and cooling of small specimens in a porcelain tube 15 mm. in diameter with quenching in water at different stages of the cooling process. The specimens are then examined under the microscope. The author uses 1 per cent. solution of nitric acid in alcohol as etching agent, and distinguishes various carbides by treatment with boiling sodium picrate or by heat tinting. The actual identification of the carbides is not very conclusive. If these various constituents could have been isolated and submitted to chemical analysis the value of the work would have been much enhanced. This has only been done in very few cases. The author, however, admits that the study is incomplete, and judging from the discordant findings of earlier workers the complete elucidation of the problem is a difficult matter. Nevertheless, the author submits, tentatively, an equilibrium diagram of the system. In any case the experimental results he has obtained will constitute a notable advance in our knowledge of the subject. The 76 photomicrographs are clear and well reproduced.

Optical Methods in Control and Research Laboratories. (London: Adam Hilger, Ltd., 75a Camden Road. Pp. 30. Price 1s. 6d. net.)

The optical methods described here are those employing spectroscopes (or spectrographs), spectrophotometers, refractometers, and polarimeters. The book is of special interest, inasmuch as very full references are given to the original sources of information concerning the apparatus dealt with. Emphasis is laid on the technical uses to which the apparatus is put. It should be of very considerable value to research laboratories. All the apparatus referred to is made in England.

A Text-Book of Organic Chemistry. By A. F. HOLLEMAN, PH.D. Fifth English Edition. Edited by A. JAMIESON WALKER, PH.D., B.A., F.I.C., assisted by O. E. MOTT., O.B.E., PH.D., F.I.C. (New York, 1920: John Wiley & Sons, Inc. London: Chapman & Hall, Ltd. Pp. xviii. + 642. Price 18s. 6d. net.)

It is given to but few authors of text-books to see their efforts so highly appreciated that translations are in demand all over the world. Professor Holleman's well-known treatise has this very enviable distinction and translations from the original Dutch have appeared in eight other languages. Actually, eight Dutch editions have now been issued and in other countries no less than thirty editions have been called for.

The domain of organic chemistry extends over so wide and so rapidly increasing an area that it is becoming more and more difficult to make a selection from the available material which will give the student a thorough grasp of the elements of the subject and so render him fitted to gain the more advanced knowledge required for research work and for the manifold technical applications of the science.

Throughout the book the author's treatment is extraordinarily well-reasoned, and the proofs of the constitutional formulæ of the various types of substances discussed are thoroughly rigid. The section on the orientation of aromatic compounds is particularly good. Sufficient space has been devoted to the aliphatic compounds, but the contents of the remainder of the book are dealt with much less fully, and naphthalene and other condensed ring bodies and heterocyclic

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types do not receive the attention that their importance merits. Nevertheless, the book contains much matter not usually met with in similar manuals, and in this connection may be mentioned the account of Tafel's work on the electro-reduction of purine derivatives.

Physico-chemical methods of investigation are being used very extensively nowadays in organic chemistry, and their importance has been fully recognised by the author who has given due attention to refraction, absorption, viscosity, etc.

The book is well printed and contains many figures, and typographical errors are very few in number. It may be warmly commended to the class of readers for which it is intended.

The Electronic Conception of Valence and the Constitution of Benzene. By HARRY SHIPLEY FRY, PH.D. Edited by PROFESSOR ALEXANDER FINDLAY. (London, 1921: Longmans, Green & Co. Pp. 297. Price 16s. net.)

This work is an addition to the series of monographs on inorganic and physical chemistry, edited by Professor Findlay. It deals largely, however, with the phenomena of aromatic organic chemistry, and it is in the reactions of the benzene nucleus that the theory finds widest application.

The book is divided into four parts. The first consists of an account of the development of the electronic theory of valency, and deals with the mode of building up electronic formulæ from the evidence furnished by oxidation, reduction, and hydrolysis. Part 2 gives an account of the electronic formula of benzene based on the Collie space formula. The Crum Brown-Gibson rule for determining whether a given benzene mono-derivative shall give a meta-di-substituted derivative or a mixture of ortho- and para-di-derivatives is treated, and the author shows that, by an extended interpretation of this rule, the apparent exceptions vanish. This section closes with a discussion of the behaviour of "free radicals" in particular of the triphenylmethyl derivatives, from the point of view of the electronic conception of valency. The third part treats of the physical properties of benzene derivatives (molecular volumes, absorption of light and fluorescence), and the book concludes wtth an account of the metal amines, followed by a bibliographical review of both support and criticism of the theory.

The book is written with lucidity, and is remarkably free from errors. The reviewer notes, however, with considerable surprise, a statement on page 29, that positive chlorine is converted to negative chlorine through the loss of electrons.

The title of the book leads one to expect some account of the theories of the structure of the atom, and of the behaviour of its constituent electrons, for any theory which postulates electrical attraction as the cause of valency must ultimately depend on the correlation of the structure of the atom with the experimental observations of chemical synthesis and reactivity. In the theory described, valency is due to mutual attraction between positively and negatively charged atoms. Negatively charged atoms are such as contain one or more electrons in excess of the number required for electrical neutrality, and positively charged atoms have a corresponding deficiency of electrons. Thus atoms exhibit positive or negative valency according as they are positively or negatively charged, each unit charge corresponding with a unit valency. The author omits all consideration of the position and properties of these valency electrons within the atom. He confines himself entirely to a consideration of the structure of molecules, the order in which their constituent atoms are united, and the electrical attraction producing this particular order. Thus each valency bond,

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represented by a line in the accepted structural formulæ of compounds, has an added significance. It is a unit Faraday tube and, as such, has direction. Since, however, any atom may exhibit either positive or negative valency and, in fact, as the author shows, may behave in $n + 1$ ways where n equals its valency, it seems that, although this theory yields ample scope for explaining previously known properties of a body, it does not enable us to prophesy the properties of any given substance, nor can it in any way elucidate the problem of chemical affinity until it is linked up with a tenable theory of the structure of the atom and the exact function of these valency electrons.

The author justly claims no more than that the theory is purely a formulative hypothesis, and in view of this it seems to the reviewer that the book fails somewhat in its purpose—"To assist . . . those reading for an Honours Degree and those undertaking research".

Nucleic Acids: Their Chemical Properties and Physiological Conduct. By WALTER JONES, PH.D. Second Edition. Monographs on Biochemistry. (London, 1920: Longmans, Green & Co. Pp. viii + 150. Price 9s. net.)

In the six years which have elapsed since this well-known monograph made its appearance much important work has been carried out on nucleic acids, and this has necessitated an increase in the size of the volume amounting to 25 per cent. The general treatment is unaltered though the discussion of the newer developments has rendered necessary a slight rearrangement of some of the matter.

The constitutional formula of yeast nucleic acid put forward by Levene and Jacobs has been modified as a result of the work of the author and his co-workers who have shown that the four nucleotides which make up the molecule are linked through the carbohydrate groups and not through phosphoric acid. All four of the nucleotides have now been isolated and the interesting discovery has been made that hydrolysis splits off phosphoric acid from the purine nucleotides very much more readily than from the pyrimidine nucleotides.

So far none of the nucleotides have been synthesised, and, perhaps for this reason, the nature of the hexose characteristic of thymus nucleic acid remains unknown. In the case of the carbohydrate of this acid only degradation products—formic and lævulinic acids—have been isolated, though *d*-ribose, the pentose of yeast nucleic acid, and of guanylic and inosinic acids has been obtained in pure condition, and its isolation has had important results since it led to the synthesis of allose and altrose. When suitable synthetic methods have been devised it may be possible by the process of trial and error to prepare a hexose nucleotide identical with one of the nucleotides of thymus nucleic acid from which the nature of the hexose group characteristic of this acid will be apparent.

The recent work of Hunter is of importance. It was already known that man differs from the lower animals including the monkey, in being unable to oxidise purines further than uric acid, but it has now been shown that the ape resembles man in this respect and a discrepancy out of harmony with evolutionary theories has thus been removed.

It may safely be stated that no paper of importance has been overlooked by Professor Jones in his account of the nucleic acids, and the book may be warmly recommended as a lucid and readable treatise on the subject. Particularly useful is the greatly extended appendix in which are given practical details for the preparation of the acids and of their products of hydrolysis.

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The Volatile Oils. By E. GILDEMEISTER and FR. HOFFMANN. Second edition by E. GILDEMEISTER. Written under the auspices of the firm of Schimmel & Co., Miltitz, near Leipzig. Authorised translation by EDWARD KREMERS, Madison Wis. (London, 1916: Longmans, Green & Co. Second Volume, pp. xx + 686. Price 32s. net.)

The appearance in English of the bulky "Schimmel," that indispensable stand-by of every worker in essential oils, will be welcomed even by those having some knowiedge of German as the condensed and sometimes rather involved style of the original often makes it somewhat difficult reading. The first volume, containing the rather elaborate historical introduction and dealing with the chemistry of the most important constituents of essential oils, appeared in 1913; the present volume treats systematically the oils found in the various plant families from the *Chroolepidaceae* to the *Zygophyllaceae* and a part of the *Rutaceae*, the remainder being reserved for the third volume. From the nature of the case, the present volume is mainly in the nature of a tabulation for reference purposes, yet the most recent advances in the study of structural formulæ have been well kept in view and the references to scientific literature are, for a technical work, remarkably up-to-date. The general get-up of the book is very pleasing, yet of a kind well calculated to stand the rather rough usage of a laboratory.

Producer Gas. By J. EMERSON DOWSON and A. T. LARTER. Fourth edition. (London, 1920: Longmans, Green & Co. Pp. 361. Price 21s. net.)

The appearance of the fourth edition of this work is in itself sufficient evidence of the place it holds in the estimation of engineers and others concerned with the gasification of fuel for industrial purposes. The first producer gas plant ever used for driving an engine was due to Mr. Dowson whose name will always be associated with the invention and its development along practical and efficient lines.

The first three chapters of the present book deal with the theory of producer gas manufacture and the chemical reactions which occur in the producer. They cover the ground clearly and adequately, and the explanation of the practical conditions necessary for the proper reactions to occur should be of considerable assistance to the designer. The use of gas producers in connection with furnace work, heating, and the operation of engines is next discussed, suction gas plants receiving a fairly extended treatment. The authors then take up the question of using bituminous coal and describe the results obtained with the Mond process as carried out on a large scale by the South Staffordshire Gas Co. Small plants for private users and manufacturing companies have now been designed to work satisfactorily with bituminous coal, and the results are said to be as good as when anthracite is used. Peat is another fuel which can now be efficiently gasified, and the authors refer to the success which has attended the operation of a 400 H.P. Crossley plant running on Irish peat, the consumption being at the rate of 2·5 lbs. of air dried peat per B.H.P. hour.

The use of producer gas as a motive power for road vehicles is briefly dealt with, the experiments of Messrs. Parker and Bamber, and of Colonel D. J. Smith being described. These are so promising, and the saving in fuel cost would be so enormous if a satisfactory portable producer plant could be devised, that one may fairly hope to see the gas producer establish itself as the power plant for,

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at any rate the heavier work of road transport. For stationary work the gas plant and the steam plant have separate fields in which they respectively excel, but in comparing them as regards fuel economy the authors rightly call attention to the heavy standby losses of a boiler plant as compared with the practically negligible coal consumption of a gas producer when not in use.

Chapters on the analysis and the calorific powers of fuels and gases are followed by some useful notes on the practical operation of gas plant, and the book closes with appendices dealing with chemical and physical information and tables. We note on page 322 that the formulæ given for the latent heat of steam are entirely wrong. In the first place the latent heat is not a linear function of the temperature, and in the second place neither of the formulæ is at all consistent with the fact that the latent heat must be zero at the critical temperature. These, however, are the only errors we noticed in the book which is of an essentially practical nature and can be recommended to all who are interested either in the design or the operation of producer gas plants.

The Fireman's Handbook and Guide to Fuel Economy. By CHAS. F. WADE. (London, 1920: Longmans, Green & Co. Pp. 84. Price 2s. 6d. net.)

The scope of this little book is fairly indicated by its title. It is a brief and sketchy outline of a fireman's duties, with hints as to the main points to be regarded in connection with the economical production of steam. Written in simple language, it can be understood by the class of operative for whom it is intended, and in so far as it is likely to encourage firemen to think about their work its publication is justified. But simplicity of language does not justify inaccuracy of statement especially in a work intended to be educational. It is not fair to any elementary student to tell him that "Heat is a form of energy that can be measured as to quantity by a thermometer," and then to expect him to understand the next sentence which reads "Different substances have different quantities of heat in them, although the temperatures may be the same". One is in fact compelled to the conclusion that the author's own studies might profitably be directed to the principles of thermodynamics, for it is clear that he does not understand them himself. Otherwise we should not be told that "The only heat of the steam that does useful work is the amount added to water to bring it just to boiling point," and "it is much more economical to work at the highest possible pressure, so that the latent heat may be as low, and the useful heat as high as possible". In these days of technical education it is very possible that some of the firemen themselves may have heard of Carnot's principle, and may know that the high latent heat of steam, instead of being disadvantageous, as Mr. Wade believes, is one of the reasons why water is such an admirable thermodynamic vehicle.

Turning to the more practical side of the book, one detects carelessness in the fact that on one page it is stated that a Lancashire boiler should be blown down at least 1½ inches per day, while on another we are told that at least 3 inches per day is necessary for the same type of boiler. As a matter of fact no definite rule can be given, for the question turns entirely upon the quantity and the nature of the make-up water. The following extraordinary statement is given as the reason for maintaining a constant water-level, "Should the water fall too low there is not enough of it to pick up the heat of the fires, a lot of which passes out to the flues and is wasted. On the other hand, with water too high there is too

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much of it to pick up the heat quickly." From the quotations we have given, it will be clear that the book is not one which can be recommended to any serious student of steam boiler operation, and one cannot help feeling the gravest doubts as to the qualifications of the author for writing an educational handbook on the subject.

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ABERDEEN: THE UNIVERSITY PRESS

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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

The Physics and Chemistry of COLLOIDS and their bearing on Industrial Questions

Report of a General Discussion

held jointly by

THE FARADAY SOCIETY

and

THE PHYSICAL SOCIETY OF LONDON

ON 25TH OCTOBER 1920

LONDON:
PUBLISHED BY HIS MAJESTY'S STATIONERY OFFICE
1921

Price 2s. 6d. Net

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PREFATORY NOTE

In view of the growing industrial importance of Colloidal Physics and Chemistry and with the intention of surveying critically the present state of knowledge as an aid to future development, the Councils of the Faraday Society and the Physical Society arranged a joint Conference on the subject which was held on the 25th October 1920.

It was realised that the Conference would fail of its desired effect if a full report of the proceedings were not published, but the two Societies concerned were unable to incur the expenditure which publication would involve. Application was accordingly made to this Department for assistance, and it was decided on the recommendation of the Advisory Council that in view of the exceptional scientific and industrial importance of the matters dealt with in the report, it should be published for the Department by H.M. Stationery Office.

It must be understood that in these circumstances the Department of Scientific and Industrial Research accepts no responsibility for the statements of opinion or fact contained in the report.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
16 and 18, Old Queen Street,
Westminster, London, S.W.1.

October, 1921.

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THE FARADAY SOCIETY

AND

THE PHYSICAL SOCIETY OF LONDON.

THE PHYSICS AND CHEMISTRY OF COLLOIDS AND THEIR BEARING ON INDUSTRIAL QUESTIONS

A GENERAL DISCUSSION

At a joint meeting of the Faraday Society and the Physical Society of London, held on Monday, October 25th, 1920, in the Hall of the Institution of Mechanical Engineers, London, a General Discussion took place on "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions."

Sir Robert Hadfield, Bart., F.R.S., President of the Faraday Society, opened the proceedings at 2.30 p.m., after which the chair was taken by **Sir William Bragg, K.B.E., F.R.S.,** President of the Physical Society of London.

A General Introduction to the Discussion, entitled "A Short Survey of the Physics and Chemistry of Colloids," was delivered by **Dr. The Svedberg,** Professor of Physical Chemistry in the University of Upsala.

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A SHORT SURVEY OF THE PHYSICS AND CHEMISTRY OF COLLOIDS

BY

DR. THE SVEDBERG,

PROFESSOR OF PHYSICAL CHEMISTRY, UNIVERSITY OF UPSALA

The science of colloids is a science of the microstructure of matter. In it is reflected the tendency of modern natural science to deal more and more intensely with the problem of structure in its full extent. In the great science of the structure of matter, the science of colloids forms the domain that lies above molecular dimensions and beneath macroscopic dimensions. In this domain we have a great number of those systems which are the basis of our material culture and the basis of life as a whole. All living beings are built up of colloids; almost all our food, our articles of clothing, our building materials, are colloids. Or, to mention some special systems, protoplasm, proteins, glue, starch, all kinds of fibres, wood, brick, mortar, cement, certain kinds of glass, rubber, celluloid, &c. The importance of colloid science for many industrial questions is, therefore, beyond all doubt.

The science of colloids is a rather young one. The field of study which it concerns has for a long time been disregarded. In order to be able to treat with success all the questions presented to us by industry, there is still much to be carried out in the department of pure colloid science. In what follows, I will try to give a short review of the scientific results so far obtained and of the problems which, in my opinion, need especial attention.

The various branches of colloid science are connected to such an extent that it is very difficult to treat the different questions separately. We will try to fix our attention on two principal problems: (1) the *formation of colloids*, and (2) the *changes of structure* in colloid systems. Connected with both these is the problem of the *properties of colloids* and the changes in these properties during the processes mentioned under (2).

The formation of a colloid may be effected in two ways, different in principle, viz., by *condensation* and by *dispersion*, according as one tries to obtain a microstructural system, a colloid, from a molecular structural or a macrostructural system.[1]

In the case of a condensation process, the degree of "graininess" or the degree of dispersion[2] will become higher as the degree of supersaturation increases; which must, of course, always precede condensation. This is the case when fogs are formed by adiabatic expansion of gases,[3] *e.g.* cloud-formation in the atmosphere, when metal colloids are prepared by condensation of metal gas from the electric arc,[4] when a slightly soluble substance, *e.g.* barium sulphate, is precipitated by means of a reaction between ions.[5] The condensation always proceeds from certain heterogenities in the medium; condensation centres or nuclei. As such nuclei, we may have particles of the substance which is to be formed by the condensation, *e.g.* precipitation of gold on small gold particles[6] when preparing gold hydrosols or gold ruby glass, or gas ions,[7] *e.g.* fog-formation in gases

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at low degrees of supersaturation, or complex molecules, *e.g.* fog-formation in gases at high degrees of supersaturation. The manner in which these nuclei are introduced into the system under condensation is of great importance for the degree of dispersion of the colloid resultant.[8] If the nuclei are not introduced into the system all at once, but gradually in the course of the condensation process, the particles will be very unequal in size.

The biologically important colloids, *e.g.*, the proteins, are evidently all formed by condensation, but no details of this process are known. The tendency towards condensation manifests itself in the fact that even the protein molecules are, from a purely chemical point of view, condensation products.[9]

In case of a dispersion process, there is always work to be performed against the surface tension or the cohesion force. Accordingly, such a process is, in contradistinction to a condensation process, a forced and not a spontaneous one. We know very little as to the relation between degree of dispersion and experimental conditions. When emulsifying fats and hydrocarbons, the surface tension may be lowered by the addition of small quantities of alkalies or soaps.[10] Grinding, in general, does not lead to a very high degree of subdivision; but it is possible to increase the latter by adding an indifferent solid diluent which can easily be dissolved and removed, leaving the disperse phase suspended in the solvent used.[11] Thus, colloid sulphur has been prepared by grinding sulphur with urea and putting the substance in water.[12] A combination of grinding and chemical effects on the material may also be used.[13] It seems that, in many cases, a prevention of the aggregation of the particles by means of suitable additions ought to render possible the preparation of high disperse systems by pure grinding.

Bubbles and foam might be regarded as a kind of colloids formed by dispersion. On spontaneously breaking up, they form new disperse systems in which the phase that was previously the continuous one becomes the non-continuous one, and *vice versâ*. The system : "soap foam — air," with the soap solution as the continuous and the air as the non-continuous phase, is transformed, on account of surface reduction *i.e.* condensation, into the system : "soap solution drops — air," with the air as the continuous phase. Mercury foam in water (produced by means of pressing water through mercury) breaks up into a mercury hydrosol partly very fine-grained.[14]

A newly-formed colloid may, immediately after its formation, undergo changes of structure of a more or less profound nature. On the other hand, it is nearly always possible to prevent the occurrence of such changes, and therefore we have a right to distinguish and investigate the *primary structure* as the direct result of the colloid-forming process.[15] Colloids with primary structure may conveniently be called *primary colloids*.

We have at our disposal several methods for the closer study of the structure. Almost every property of a colloid depends on the structure, and therefore, conversely, from the study of the properties of colloids we may draw conclusions as to their structure.

The most important and most obvious means is the microscope and the ultramicroscope.[16] With their aid, it is often possible to settle whether the colloid under investigation is of a grainy structure, *e.g.* a colloid gold solution in water, a gold hydrosol, or of a foamy structure, *e.g.* high disperse soap foam, or of a fibrous structure, *e.g.* soap solutions of certain concentrations. The number and

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approximate size of the discontinuities, *e.g.* the particles, may also be determined in this way. One may, for instance, count in the ultramicroscope the number of particles observed in a certain volume of gold hydrosol, and by means of analysis determine the content of gold present in the sol. From these figures we get the mass and approximate size if, for instance, we make the assumption that they are spherical. On the other hand, the ultramicroscope gives little or no information about the form or structure of the particles.[17]

A means of deciding whether the particles are symmetrical is to be found in the study of the behaviour of the colloids in magnetic or electric fields.[18] Non-symmetrical particles are oriented by such fields and thereby impart to the colloid a certain, though in general very slight, degree of double refraction, which may easily be measured with great accuracy. In this way, we have been able to settle that the particles in common sulphur hydrosols, prepared by oxidation of hydrogen sulphide, are spherical; but sulphur hydrosols, prepared by grinding sulphur with urea, are unsymmetrical. The particles in gold hydrosols prepared by reduction are unsymmetrical to a high degree.[19]

Two other optical properties, viz., the light absorption and its accompanying phenomena, the scattering and polarisation of light—the Tyndall phenomenon—may also in certain cases be used for structure studies.[20] Theory, as well as practice, proves that these phenomena are, for instance, dependent to a great extent on the degree of dispersion of the sol. The form and structure of the particles also influence the said properties, but in a manner hitherto unknown. The emission of light from illuminated particles especially—the Tyndall light cone—varies to a great extent with the size of the particles or the degree of dispersion.[21] Colloid solutions that contain very small particles, *e.g.* Faraday's gold hydrosols, give only a slight emission; the light cone is scarcely visible. Those with large particles, *e.g.* gold sols made from Faraday's gold sols by allowing the particles to grow in a reduction mixture, emit very much light; the Tyndall cone is very prominent. The optical properties of the particles also play a great part. Thus metal particles emit much light, particles of silicic acid or of gelatin only a little.

The resistance exerted on the particles by the surrounding medium when they move under the influence of a force is a means of investigation that is now often used for the determination of the size of the particles. In some cases, *e.g.* when a sol is filtered through a membrane of collodium or gelatine (ultrafiltration[22]), the connection between the resistance and the size of the particles is not known in detail, but we are justified in assuming that the resistance rises with the size of particles. The small particles are more rapidly pressed through the filter than the large ones.[23] Certain kinds of filters transmit molecularly dissolved substances, but not colloids; an important method of separation, especially in biochemistry. If a colloid is separated from a great quantity of dispersion medium by such a membrane, the molecularly dissolved substances—the crystalloids—diffuse through the membrane, leaving a colloid of a purer state—Graham's dialysis.[24] If the particles are spherical and move through a liquid, the resistance is $6\pi\eta rv$, where η is the viscosity, r the radius and v the velocity. If the force that causes the movement is known, *e.g.* gravity, the radius may be calculated.

Thus, by measuring the velocity of sedimentation, the radius can be found.[25]

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We have

$$r = \sqrt{\frac{9\eta v}{2(s_1 - s_2)g}}$$

where s_1 is the specific gravity of the particle, s_2 that of the liquid, and g the gravity constant.

Even when no exterior forces are acting, the particles in a colloid solution are in movement because of the impacts from the surrounding molecules. This is the so-called Brownian movement, which has attracted so much attention of late.[26] According to the kinetic theory of the Brownian movement, which has been fully confirmed experimentally, each particle, whatever its size and nature, has the same translatory energy as a molecule, *i.e.* $\frac{3RT}{2N}$, where R is the gas constant, T the absolute temperature, and N the Avogadro constant. Because of the resistance of the surrounding medium, the mean value of the square of the distance traversed in the time t by the particle is $2Dt$, where D, the diffusion constant of the particles, has the value $\frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$. Thus, if the displacement of the particle is measured the radius may be found. In certain cases it is more convenient to measure D directly and then calculate r by means of this experimental value.

Owing to the fact that the size of the particles is rather great in comparison with that of the molecules, colloids diffuse very slowly compared with crystalloids. As a matter of fact, Graham, the founder of colloid chemistry, regarded this property as the fundamental difference between colloids and crystalloids. We know now that between colloids and crystalloids—so very different in their extremes—there exist all degrees of transition forms, and therefore all degrees of diffusibility.

The size of particles may also be determined by measuring the sedimentation equilibrium, *i.e.*, the distribution of the number of particles per c.c. under the joint influence of gravity and the Brownian movement. In this equilibrium, the concentration of the colloid diminishes exponentially with increasing height, as is the case with the atmosphere surrounding the earth.

We have

$$n_2 = n_1 \cdot e^{-\frac{N}{RT} \cdot \frac{4}{3}\pi r^3 (s_1 - s_2) g (x_1 - x_1)}$$

where n_1 is the number of particles at the height x_1, n_2 that at the height x_2.

Hence

$$r = \sqrt[3]{\frac{RT}{N} \cdot \frac{ln \frac{n_1}{n_2}}{\frac{4}{3}\pi(s_1 - s_2)g(x_2 - x_1)}}.$$

The osmotic pressure of a colloid solution is determined, as far as the colloid in it is concerned, only by the number of particles per c.c.(n).

We have

$$p = \frac{RT}{N} \cdot n.$$

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Consequently, the osmotic pressure is a measure of the degree of dispersion. The osmotic pressure of a colloid is often determined by means of a common osmometer, provided with a membrane permeable to crystalloids, but impermeable to the colloid particles.[27] Now, however, owing to ion adsorption, the particles are, in most cases, surrounded by an electric double-layer of ions, and the colloid thus acts as an electrolyte, one ion of which is able to penetrate the membrane, but not the other. This causes complications. A so-called membrane equilibrium is formed, and the osmotic pressure found is not a real measure of the structure of the colloid.[28]

Owing to the Brownian movement, the number of particles in every small volume of a sol undergoes spontaneous and incessant fluctuations. Hence the value of every property of the colloid in the small volume fluctuates.[29]

We have

$$n = \frac{e^{-\nu}\nu^n}{\underline{|n}}.$$

where n is the momentary value of the number of particles in the small volume v and ν the mean value.

This phenomenon, predicted by the kinetic theory for colloidal as well as for molecular solutions, has been the subject of extensive investigations. The results are of importance because they show that Boyle's law holds good very exactly for dilute colloid solutions, and because of the light they have thrown on the applicability of the probability calculus to a natural phenomenon. From these studies we have also obtained a deeper comprehension of the conception of entropy. For they have shown, in a direct and experimental way, that the law of the incessant growth of entropy only holds for macroscopic systems.[30]

It often occurs that the particles of a colloid are too small to be measured directly, *e.g.* by means of the ultramicroscope or by determining the velocity of sedimentation. In some of these cases one can overcome the difficulty by depositing gold on the particles, thus increasing their size.[31] This method has already been applied to sols of almost all the metals and to sols of some sulphides.[32] If the quantity of gold on a particle is known, it is easy to calculate the radius in the usual manner.

In most colloid solutions and precipitates there are particles of various sizes, and the investigator should, of course, be able to determine not only the mean size, but also the real structure of the sol, *i.e.* the law governing the distribution of the various sizes of particles.[33] Among the phenomena reviewed above only the velocity of sedimentation, the sedimentation equilibrium, and the Brownian movement have been used in studying the distribution of the size of the particles. On the basis of the former phenomenon just mentioned a method has been worked out which has already provided us with much valuable information as to the formation of the various particles in colloids and the agglomeration processes taking place in them.[34]

Finally we will consider two phenomena, the study of which does not, it is true, enable us to carry out direct measurements of the structure, but which, in spite of that, are of great interest in judging of the structure of colloids, viz., the viscosity[35] on the one hand, and, on the other, the adsorption[36] and the accompanying phenomena, viz., the cataphoresis[37] and the electric endosmose.[38]

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The viscosity of a sol depends, in a manner not yet known, on the size of the particles, the concentration, &c., but above all on the nature of the particles. Some sols, *e.g.* metal hydrosols, suspensions of barium sulphate (Case 1) have a viscosity only slightly greater than that of water, but others, *e.g.* silicic acid hydrosol, oil emulsion, gelatin solution (Case 2) have a viscosity many times greater than that of water. From the fact that suspensions with undoubtedly solid particles come under Case 1 and emulsions with undoubtedly fluid particles come under Case 2, the conclusion has been drawn that the fine-grained colloids under Case 1 also contain solid particles and those under Case 2 fluid ones. If this be the case, measurements of the viscosity would be a capital means of ascertaining the state of aggregation of the substance of the particles. Recent investigations indicate, however, that the case is far more complicated. Small particles probably have relatively thicker water-coverings than greater particles, and, accordingly, the viscosity is higher in a fine-grained colloid than in a coarser one, provided the two sols have particles of the same material and are of the same concentration by weight (*e.g.*, sulphur hydrosols). When the potential difference between particles and fluid is altered the thickness of the water-coverings should alter and, as a matter of fact, the viscosity is altered too. As the water-covering increases, the particle will act more and more like a drop of fluid in relation to the surrounding medium and will, therefore, as far as the viscosity is concerned, approach more and more to the limiting case which is represented by an oil emulsion.[39]

The phases—two or more in number—in a disperse system have a contact surface very large relatively to the volume of the system. It is obvious that in such circumstances adsorption plays a prominent *rôle*. The adsorption of different substances differs in strength. If an electrolytically-dissociated salt is adsorbed, cations and anions are, of course, brought together at the contact surface in equal numbers, but the adsorption of the particles in relation to cations and anions is most often unequal, inasmuch as one is present in excess nearest to the surface of contact and the other in excess some way out in the liquid[40]. The result is the formation of an electrical potential difference, a so-called adsorption potential difference or an electrical double-layer. Because of this the disperse phase, when exposed to the influence of an electric field, will migrate towards one of the poles, provided it is freely movable, as in the case of a colloid solution (cataphoresis). If the disperse phase is immovable the liquid will move in the opposite direction (electrical endosmose). By measuring the velocity of migration of the particles or the liquid under various conditions we are able to study the changes in the difference of potential and thereby in the adsorption. At least at low concentrations the adsorption may be expressed by the formula

$$y = \alpha \cdot c^{\beta}$$

where y is the amount of substance adsorbed per gr. adsorbent, c the concentration in the solution of the substance adsorbed, and α and β constants depending on the nature of both. Now, as a rule, it happens that for the two ions of a salt both α and β have different values, *e.g.*

$$\alpha \text{ cation} < \alpha \text{ anion}$$
$$\beta \text{ cation} > \beta \text{ anion}$$

In the example chosen the disperse phase will with increasing adsorption become more and more negative in relation to the dispersion

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medium. This charge reaches a maximum and decreases to zero, at the point where the adsorption isotherms intersect, then becomes positive and increases again[41].

The changes of state which may occur in a disperse system, a colloid, are essentially changes of structure[42]. Of course, purely chemical reactions, too, are to be taken into consideration, but they do not play such a prominent part here as in the molecular structural systems. The greater number of the disperse systems, and those of greatest importance too, are the ones whose disperse phase is embedded in the other phase in the form of particles; in the sequel we will only mention the changes of state in such systems. The most important change of state is the uniting together of the single particles (primary particles) into aggregates (secondary particles). Such an aggregation often occurs directly after the formation of the particles. It may stop for various reasons after the aggregates have reached a certain size. The result is a colloid with complex particles —a *secondary colloid*. If the aggregation goes on further we may have two extreme possibilities—with many transition forms.

FIRST CASE: one or more of the following factors dominate, viz. :—

(1) Low hydration of the particles.
(2) Low number of particles per unit volume.
(3) Great difference in specific gravity between particles and liquid.
(4) Violent stirring of the system.

The characteristic of this case is that no bridges are formed between the aggregates and that, in consequence of this, they fall to the bottom after having grown sufficiently; *the colloid is precipitated* (*e.g.* coagulation of a gold hydrosol by the addition of hydrochloric acid).

SECOND CASE: one or more of the following factors dominate, viz. :—

(1) High hydration of the particles.
(2) High number of particles per unit volume.
(3) Small difference in specific gravity between particles and liquid.
(4) No stirring of the system.

In this case bridges are formed between the aggregates, and the particles arrange themselves into a three-dimensional network throughout the system: *the colloid gelatinizes* (*e.g.* the coagulation of a sol of silicic acid by the addition of hydrochloric acid, the setting of a warm gelatine solution when cooling). Owing to capillary forces the liquid is kept in the network with great strength. Measurements have shown that the liquid is under a pressure of several hundred atmospheres. In many respects, therefore, the gelatinized colloid acts as a solid.

There exist numerous transition forms between these two extreme cases. If the particles are not bound together by bridges into a solid, but still reach macroscopical size and possess a certain loose structure, one speaks of *flocculation of the colloid* (*e.g.* coagulation of ferric hydroxide hydrosol by addition of ammonia). It may be doubted, however, if such flocculent suspensions are not to be regarded as fragments of a gel of little mechanical resistance shattered by the stirring of the liquid. Several observations support the view that there is in all colloids a certain tendency towards the formation of

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a network structure, the network being, however, in such systems as approach CASE 1, very easily destroyed by movements in the liquid. In CASE 1 the Brownian movements alone of the particles should suffice.

The most important cause of the aggregation of the particles is the decrease or the disappearance of the difference of potential between particle and liquid. This may be effected by altering the ion adsorption. Hence one of the most important means of bringing about aggregation or disaggregation is : *addition or removal of ions.* Because of the opposite electric and coagulating action of anion and cation and their difference of adsorption there will always exist, for certain electrolytes in relation to a certain colloid, a domain of concentration within which they have a disaggregating action. If a solely aggregating electrolyte is added to a colloid in increasing doses (*e.g.* hydrochloric acid to a gold hydrosol), the velocity of aggregation first rises rapidly with concentration, then more slowly and reaches a constant maximum value[43]. Let us make the assumption that within the latter region *every* mutual approach of two particles to a certain limit leads to aggregation, but within the former region only a certain *fraction* of those approaches. Then it is possible to develop, on the basis of the laws of the Brownian movements alone, a mathematical theory for the kinetics of aggregation. The formulæ for the decrease in the number of single particles (primary particles), and for that in the total number of particles (primary particles + aggregates) have been verified experimentally.[44]

We have—

$$\nu_1 + \nu_2 + \nu_3 + \ldots = \frac{\nu_0}{1 + \beta t}$$

$$\nu_1 = \frac{\nu_0}{(1 + \beta t)^2}$$

where—

ν_0 = original number of particles.
ν_1 = number of single particles after the time t.
ν_2 = number of double particles after the time t.
ν_3 = number of triple particles after the time t.
$\beta = 4\pi DR\nu_0$.
D = the diffusion constant.
R = the distance to which the particles must approach if there is to be any aggregation.

With regard to the aggregation by electrolytes it has, in addition, been found that inorganic ions of the same valency generally aggregate equally strongly if added in equivalent amounts[45]. This is due to some extent to their being nearly equally strongly adsorbed. When the valency of the aggregating ion increases the aggregating effect rises very rapidly[46]. The concentrations of the ions $K\cdot$ $Ba\cdot\cdot$ $Al\cdot\cdot\cdot$ required to aggregate particles of As_2S_3 to the same degree show the mutual relations : 1, 1/20, 1/1000. Thus the three-valent $Al\cdot\cdot\cdot$ has an aggregating power 1,000 times greater than the mono-valent $K\cdot$. These circumstances are closely related to the course of the adsorption isotherm, but are not yet quite clear[47].

The aggregation may be reversible or irreversible, *i.e.*, in certain cases disaggregation may be effected, in others not. Some colloids (*e.g.*, metal hydrosols) are difficult to disaggregate, others (*e.g.* sulphur hydrosols) are easy. Certain ions nearly always bring about

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irreversible, others reversible aggregation. The question of irreversible or reversible coagulation is probably closely connected with that of the hydration of the particles. Thus particles which hold much water around them are easily disaggregated. The water-covering prevents the particles from uniting too closely together.

The aggregating effect of an electrolyte may often be reduced to a very great extent by the addition of a small quantity of a suitable colloid of another kind only slightly sensitive to electrolytes, a so-called protective colloid, *e.g.* gelatine to a gold hydrosol.[48] As a rule the electric charge of the protective colloid should be of the same sign as that of the colloid to be protected. The mechanism of this protecting action is still but very incompletely known. Most probably the particles of the protective colloid become attached to the particles of the other colloid and the aggregate resulting from this obtains a good deal of the stability towards electrolytes which characterises the protective colloid. Colloids of opposite electric charge precipitate each other mutually (*e.g.* the negative Sb_2S_3 and the positive Fe_2O_3) provided there is not too great an excess of either of them, in which case no precipitation will occur[49]. This is obviously entirely analogous to the action of the ions. Such mutual colloidal reactions are of great importance in the economy of nature and in industry.

In the preparation of easily aggregated colloids a protective colloid is often added in order to maintain the primary structure. Thus the particles of a metal hydrosol, if formed in the presence of a small quantity of a protective colloid, are kept apart even when the sol is evaporated to dryness. The dry substance can be redissolved in water without any perceptible change of structure taking place (*e.g.* commercial colloid silver[50]).

A change of structure that plays a part, formerly a little overrated, in colloid solutions with comparatively easily soluble particles is the growth of the larger particles at the expense of the smaller ones.[51] In a suspension of calcium sulphate this change of structure is clearly visible, but in the more sparingly soluble barium sulphate the process goes on at an extremely slow rate.[52] Formerly, aggregation, especially the irreversible process, was often interpreted as a recrystallisation. In irreversible aggregates as well as in compressed powders there gradually take place association and crystallisation phenomena which may greatly change the structure of the system (*e.g.* silver crystals in sediments from silver colloids).

Processes of the latter kind play a prominent part, especially in gelatinized colloids. On the whole a great variety of changes in structure and accompanying processes may occur in gels. When gradually deprived of water the gel of silicic acid, for instance, goes through a series of states, some of which differ rather decidedly from others.[53] The nature of these processes is not yet known. A gelatine gel probably consists of particles with a high percentage of "dry substance" and a liquid with a low percentage. In sol-formation water is supposed to pass over from the liquid to the particles, the particle-associations being thereby disintegrated; in the gel-formation the particles lose water.[54]

In the study of the changes of structure and of the properties of secondary sols and gels we use, at least to some extent, the same methods as in the study of sols. Thus aggegration may be followed in the ultramicroscope, by sedimentation observations, by means of measuring the light-adsorption, the double refraction in magnetic and electric fields, the viscosity. The most reliable method consists,

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of course, in direct countings of the particles in the ultramicroscope. But it is not always possible to carry out these countings. The viscosity is a very sensitive indicator of changes in structure, especially within the organic colloids. The values we arrive at when measuring the viscosity of an aggregating colloid are, however, dependent to a great extent on the state of current in the system and, consequently, on the kind of method employed for the measurement. The microscopic aggregation process is accompanied by a building up of a macroscopic network and the mechanical resisting power of this network determines, to a considerable degree, the viscosity measured by the experimenter. The aggregation may lead to the formation of secondary particles of a more or less high degree of dissymmetry. This can be studied by measuring the change which the double refraction of the sol in a magnetic field undergoes during the progress of aggregation.

The study of the structure of gels is a rather difficult one.[55] The particles of most gels do not contrast optically to any great extent with the surrounding medium and consequently the ultramicroscope is not able, as a rule, to make their primary particles visible.[56] Moreover, these are often packed together so closely that they cannot be distinguished from one another optically. On the other hand, we have been able to study with more success the macroscopic properties of the gels in chemical and physical respects. The elastic gels, especially gelatine, collodion, celluloid, rubber, &c., play a prominent part in industry and their investigation is therefore a matter of great importance.[57]

With these few remarks concerning the structure of gels I must close my review. It is very incomplete—I am aware of the fact. The following discussion will, however, I am sure, fill up many of the blanks left open by me. In cases where our knowledge is still undeveloped, I trust the discussion will give valuable suggestions and help us to put the problems to new and crucial tests.

Bibliography

Books dealing with the whole subject or important parts of it:

van Bemmelen, *Die Absorption*, 1911.
Bechhold, *Die Kolloide in Biologie und Medizin.*
Bredig, *Anorganische Fermente*, 1901.
British Association Reports, 1917, 1918 and 1919.
Burton, *Colloid Solutions*, 1916.
Cotton and Mouton, *Les ultramicroscopes et les objets ultramicroscopiques*, 1906.
Faraday Society, *Trans.*, 1913.
Freundlich, *Kapillarchemie*, 1909.
Hatschek, *Physics and Chemistry of Colloids*, 1919.
Hatschek, *Laboratory Manual of Colloid Chemistry*, 1920.
Kohlschütter, *Die Erscheinungsformen der Materie*, 1917.
Lottermoser, *Anorganische Kolloide*, 1901.
Müller, *Allgemeine Chemie der Kolloide*, 1907.
Wo. Ostwald, *Colloid Chemistry*, 1919.
Wo. Ostwald, *Praktikum der Kolloidchemie*, 1920.
Perrin, *Brownian Movement and Molecular Reality*, 1910.
Svedberg, *Herstellung kolloider Lösungen*, 1909.
Svedberg, *Die Existenz der Moleküle*, 1912.
von Weimarn, *Grundzüge der Dispersoidchemie*, 1911.
Zsigmondy, *Chemistry of Colloids*, 1917.
Zsigmondy, *Kolloidchemie*, 1918.

[1] Svedberg, *Nova Acta*, Upsala, ser. 4, vol. 2, No. 1, p. 3, 1907.
[2] Wo. Ostwald, *Koll. Zeitschr.*, **1**, 294, 1907.
[3] C. T. R. Wilson, *Phil. Trans.*, **A. 189**, 265, 1897; **A. 192**, 403, 1899; **A. 193**, 289, 1900.

Digitized by Google

[4] Bredig, *loc. cit.*; Svedberg, *loc. cit.*; *Koll. Zeitschr.*, **24**, 1, 1919; *Meddel. Nobelinst.*, Stockholm, **5**, No. 10, 1919; Kohlschütter, *loc. cit.*, p. 167.

[5] von Weimarn: *loc. cit.*, p. 54; *Zur Lehre von den Zuständen der Materie*, p. 164, 1914; Odén, *Arkiv för Kemi*, Stockholm, **7**, No. 26, 1920; *Koll. Zeitschr.*, **26**, 100, 1920.

[6] Zsigmondy, *Zur Erkenntnis der Kolloide*, p. 128, 1905.

[7] C. T. R. Wilson, *loc. cit.*

[8] Zsigmondy, *Kolloidchemie*, p. 144; Kohlschütter, *loc. cit.*, p. 167.

[9] E. Fischer, *Ber. Deutsch. chem. Ges.*, **39**, 1, 530, 1906.

[10] Donnan, *Zeitschr. phys. Chem.*, **31**, 42, 1899; Hatschek, *Brit. Assoc. Report*, 1918, p. 16.

[11] v. Weimarn, *Grundzüge, loc. cit.*, p. 82.

[12] Pihlblad, *Lichtabsorption und Teilchengrösse, Dissert.*, Upsala, 1918.

[13] Küzel, *Österreich. Patent, Kl.*, 12b, No. A. 2573, 1906; Lottermoser, *Koll. Zeitschr.*, **2**, 347, 1908; Wedekind, *Koll. Zeitschr.*, **2**, 289, 1908; Bancroft, *Brit. Assoc. Report*, 1918, p. 6.

[14] Nordlund, *Quecksilberhydrosole, Dissert.*, Upsala, 1918. p. 18.

[15] Mecklenburg, *Zeitschr. anorg. Chem.*, **74**, 262, 1912; Odén, *loc. cit.*

[16] Siedentopf and Zsigmondy, *Annal. Phys.*, 4, **10**, 1, 1903; Zsigmondy, *Kolloidchemie*, p. 12; Burton, *Colloid Solutions*, p. 28.

[17] Cotton and Mouton, *loc. cit.*, p. 166.

[18] Cotton and Mouton, *loc. cit.*, p. 172.

[19] Dieselhorst and Freundlich, *Phys. Zeitschr.*, **16**, 419, 1915; **17**, 117, 1916; Bergholm and Björnståhl, *Phys. Zeitschr.*, **21**, 137, 1920; Björnståhl, recent investigations not yet published.

[20] Faraday: *Phil. Mag.*, 4, **14**, 402, 1857; *Proc. Roy. Inst.*, **2**, 310 and 444, 1854–58; Tyndall, *Proc. Roy. Soc.*, **17**, 223, 1868; Rayleigh, *Phil. Mag.*, 4, **41**, 107 and 447, 1871; 5, **47**, 375, 1899; J. J. Thomson, *Recent Researches*, p. 449, 1893; Garnett, *Phil. Trans.*, **A. 203**, 385, 1904; **205**, 237, 1906; Mie, *Annal. Phys.*, 4, **25**, 377, 1908; Gans and Happel, *Annal. Phys.*, 4, **29**, 277, 1909; Linder and Picton, *Journ. Chem. Soc.*, **61**, 114, 1892; **67**, 63, 1895; Svedberg, *Die Existenz der Molekyle*, p. 5; Pihlblad, *Lichtabsorption*.

[21] Abney and Festing, *Proc. Roy. Soc.*, **40**, 378, 1886; Mecklenburg, *Koll. Zeitschr.*, **14**, 172, 1914; **15**, 149, 1914; **16**, 97, 1915; Rinde, recent investigations not yet published.

[22] Malfitano, *Comptes rend.*, **139**, 1221, 1904.

[23] Bechhold, *Zeitschr. phys. Chem.*, **60**, 257, 1907

[24] Graham, *Phil. Trans.*, **151**, 183, 1861; Zsigmondy and Heyer, *Zeitschr. anorg. Chem.*, **68**, 169, 1910; Walpole, *Biochem. Journ.*, **9**, 284, 1915.

[25] Stokes, *Cambr. Phil. Trans.*, **8**, 287, 1845; **9**, 8, 1851; Perrin, *Compt. rend.*, **147**, 475, 1908; Nordlund, *Arkiv för Matematik*, Stockholm, **9**, No. 13, 1913.

[26] Brown, *Phil. Mag.*, 4, 161, 1828; Einstein, *Annal. Phys.*, 4, **17**, 549, 1905; **19**, 371, 1906; v. Smoluchowski: *Annal. Phys.*, 4, **21**, 756, 1906; *Phys. Zeitschr.*, **17**, 557 and 587, 1916.; Svedberg: *Zeitschr. Elektrochem.*, **12**, 853 and 909, 1907; *Jahrb. Radioaktivität*, **10**, 467, 1913; Perrin, *Compt. rend.*, **146**, 967, 1908; *Brownian Movement*; Nordlund, *Zeitschr. phys. Chem.*, **87**, 40, 1914; Westgren, *Zeitschr. anorg. Chem.*, **93**, 231, 1915.

[27] Duclaux, *Journ. Chim. Phys.*, **5**, 29, 1907; **7**, 429, 1909; Bayliss, *Proc. Roy. Soc.*, **81**, 269, 1909.

[28] Donnan, *Zeitschr. Elektrochem.*, **17**, 572, 1911; Donnan and Harris, *Journ. Chem. Soc.*, **99**, 1554, 1911; Moore and Parker, *Amer. Journ. Physiol.*, **7**, 262, 1902; Moore and Roaf, *Biochem. Journ.*, **2**, 34, 1907.

[29] v. Smoluchowski, *Annal. Phys.*, 4. **25**, 205, 1908; Svedberg, *Zeitschr. phys. Chem.*, **73**, 547, 1910; **77**, 145, 1911; Westgren, *Arkiv för Matematik*, Stockholm, **11**, No. 14, 1916; **13**, No. 14, 1918.

[30] v. Smoluchowski, *Physikal. Zeitschr.*, **13**, 1069, 1912.

[31] Zsigmondy, *Zeitschr. phys. Chem.*, **56**, 65, 1906; Westgren, *Zeitschr. anorg. Chem.*, **93**, 151, 1915.

[32] Börjeson, *Koll. Zeitschr.*, **27**, 18, 1920.

[33] Svedberg and Estrup, *Koll. Zeitschr.*, **9**, 259, 1911; Westgren, *Zeitschr. anorg. Chem.*, **94**, 193, 1915.

[34] Odén: *Proc. Roy. Soc.*, Edinburgh, **36**, 219, 1916; *Koll. Zeitschr.*, **26**, 100, 1919.

[35] Hatschek: *Brit. Assoc Report*, 1917, p. 21; *Koll. Zeitschr.*, **7**, 301, 1910; **8**, 34, 1911; **12**, 238, 1913; Einstein, *Annal. Phys.*, 4, **19**, 289, 1906; 4, **34**, 591, 1911; Odén, *Zeitschr. phys. Chem.*, **80**, 709, 1912; v. Smoluchowski, *Koll. Zeitschr.*, **18**, 190, 1916.

[36] van Bemmelen, *Die Absorption*; Freundlich, *Kapillarchemie*; Arrhenius, *Meddel. Nobelinst.*, Stockholm, **2**, No. 7, 1911; Marc, *Zeitschr. phys. Chem.*, **81**, 641, 1913.

Digitized by Google

[37] Linder and Picton, *Journ. Chem. Soc.*, **61**, 148, 1892; Hardy, *Journ. Physiol.*, **24**, 288, 1899; Lottermoser and v. Mayer, *Journ. prakt. Chem.*, 2. **56**, 241, 1897; Burton, *Phil. Mag.*, 6, **211**, 425; **12**, 472, 1906; Lewis, *Koll. Zeitschr.*, **4**, 211, 1909.

[38] Quincke, *Annal. Phys.*, 2, **113**, 513, 1861; Perrin, *Journ. Chim. Phys.*, **2**, 601, 1904; Bancroft, *Trans. Amer. Electrochem. Soc.*, **21**, 233, 1912; Briggs: *Journ. Phys. Chem.*, **21**, 198, 1917; **22**, 256, 1918; *Brit. Assoc. Report*, 1918, p. 26.

[39] Hatschek: *Koll. Zeitschr.*, **11**, 280, 1912; **12**, 240, 1913; *Biochem. Journ.*, **10**, 325, 1916; Arrhenius, *Meddel. Nobelinst.*, Stockholm, **3**, No. 13, 1916.

[40] Freundlich, *loc. cit.*, p. 245; Pauli: *Hofmeisters Beitr.*, **6**, 233, 1905; *Biochem. Zeitschr.*, **52**, 369, 1913.

[41] Odén, *Arkiv, loc. cit.*, p. 7.

[42] Burton, *Colloid Solutions*, p. 145; Zsigmondy, *Kolloidchemie*, p. 66; Odén, *Nova Acta*, Upsala, ser. 4, Vol. 3, No. 4, 1913; Bancroft, *Brit. Assoc. Report*, 1918, p. 2.

[43] Zsigmondy, *Göttinger Nachr.*, 1917.

[44] v. Smoluchowski, *Zeitschr. phys. Chem.*, **92**, 129, 1917; Zsigmondy, *Kolloidchemie*, p. 71; Westgren and Reitstötter, *Zeitschr. phys. Chem.*, **92**, 750, 1918; Westgren, *Arkiv för Kemi*, Stockholm, **7**, No. 6, 1918.

[45] Hardy, *loc. cit.* and *Zeitschr. phys. Chem.*, **33**, 385, 1900.

[46] Schulze, *Journ. prakt. Chem.*, 2, **25**, 431, 1882; Linder and Picton, *Journ. Chem. Soc.*, **67**, 63, 1895; **87**, 1906, 1905.

[47] Freundlich, *Zeitschr. phys. Chem.*, **44**, 129, 1903.

[48] Zsigmondy, *Kolloidchemie*, p. 142.

[49] Linder and Picton, *Journ. Chem. Soc.*, **71**, 568, 1897; Lottermoser, *loc. cit.*; Biltz, *Ber. Deutsch. chem. Ges.*, **37**, 1111, 1904; Bancroft, *Journ. Phys. Chem.*, **18**, 555, 1914.

[50] Paal, *Ber. Deutsch. chem. Ges.*, **35**, 2224, 1902.

[51] Wo. Ostwald, *Zeitschr. phys. Chem.*, 34. 496, 1900; Hulett and Allen, *Journ. Amer. Chem. Soc.*, **24**, 667, 1902.

[52] Odén, *Arkiv, loc. cit.*

[53] van Bemmelen, *Die Absorption.*

[54] *Cf.* Hatschek, *Physics and Chemistry of Colloids*, p. 54.

[55] Bütschli, *Untersuchungen, &c.*, Heidelberg, 1900; Hardy, *Zeitschr. phys. Chem.*, **33**, 326, 1900; Pauli, *Der kolloide Zustand und die Vorgänge in der lebenden Substanz*, Braunschweig, 1902.

[56] Zsigmondy, *Kolloidchemie*, p. 104; Bachmann, *Zeitschr. anorg. Chem.*, **73**, 125, 1911.

[57] Rodewald, *Zeitschr. phys. Chem.*, **24**, 193, 1897; Liesegang, *Chemische Reaktionen in Gallerten*, Düsseldorf, 1898; Posnjak and Freundlich, *Kolloidchem. Beih.*, **3**, 417, 1912; Hatschek: *Physics and Chemistry of Colloids*, p. 63; *Brit. Assoc. Report*, 1918, p. 21.

Note on **Prof. Svedberg's** paper received from **Prof. E. F. Burton** (University of Toronto):—

It should be pointed out that Perrin's experiments on the variation of the distribution of colloidal particles with height were carried out for only very small heights and the resulting formula can be true only for a small distance near the surface. Substitution of the values of the constants in the equation—

$$n_2 = n_1 \cdot e^{-\frac{N}{RT} \cdot \frac{4}{3} \pi r^3 (s_1 - s_2) g (x_2 - x_1)}$$

with a value of, say, 25 cms. for $(x_2 - x_1)$, will show the unreality of the law for such distances. Perrin neglects altogether the mutual effect of the particles due to their charges.

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The following contribution to the General Discussion was received from **Dr. Wolfgang Pauli** (Vienna) in response to an invitation:—

THE GENERAL STRUCTURE OF COLLOIDS

BY

WOLFGANG PAULI

A careful physico-chemical analysis of ferric hydroxide sol, more particularly by means of potentiometric determination of the ion concentrations, had shown that it could, in the main, be considered as a complex salt of the composition—

$$x\ \mathrm{Fe(OH)_3}\ y\ \mathrm{Fe}\ |\ \mathrm{An}$$

where " An " represents the anion of the ferric salt from which the sol had been prepared. From this structure the properties of ferric hydroxide sol may be deduced without any special assumptions and without introducing the concept of adsorption.

In the course of the last few years my collaborators, Mrs. Mona Adolf and Johann Matula, and myself have succeeded in extending the experiments to a number of oxy-salts and sols of polyvalent metals, and have thus arrived at a more general conception of colloids involving a more intimate connection with chemistry than has hitherto been possible.

To quote one example, a whole series of ionising complex molecules can be shown to exist in zirconium oxychloride ($\mathrm{ZrOCl_2}$), by determining the H and Cl ion concentration (electrometrically), the conductivity, the freezing point and the transport numbers, of which I will mention a few only :

$$\mathrm{Zr(OH)_4.Zr(OH)_4.ZrOCl_2.\overset{+\,+}{Zr}O\ |\ \overset{-\,-}{Cl_2}}$$

$$\mathrm{Zr(OH)_4.ZrOCl_2.\overset{+\,+}{Zr}O\ |\ \overset{-\,-}{Cl_2}}$$

$$\mathrm{Zr(OH)_4.\overset{+\,+}{Zr}O\ |\ \overset{-\,-}{Cl_2}}$$

In addition to positive groups there occur also negative groups of a complex zirconic acid, such as—

$$\mathrm{Zr(OH)_4.ZrOCl_2.\overset{-\,-}{Cl_2}\ |\ \overset{+\,+}{H_2}}$$

which can be combined with the above positive complexes.

The usual aluminium hydroxide sol, when prepared from aluminium acetate, proves to be an aluminium mono-acetate—

$$\mathrm{Al(OH)_2CH_3COO}$$

which is largely dissociated hydrolytically and in which the complex ions $\mathrm{3Al(OH)_3.\overset{+}{Al}(OH)_2\ |\ \overset{-}{CH_3}COO}$ have grouped themselves into colloid particles.

We have furthermore been able to prepare from $\mathrm{AlCl_3}$ the following transitions to aluminium hydroxide sol—

$$\mathrm{Al(OH)Cl_2};\ \mathrm{Al(OH)_2Cl};\ \mathrm{2Al(OH)_3Al(OH)_2.Cl}.$$

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In all cases the metal hydroxides show a tendency to transform themselves, by the addition of an ionogenic molecule, into charged particles, an aggregation of which forms the colloid complex.

We also demonstrated the interesting fact that, with increasing concentration of $Al(OH)_3$, the aluminium oxy-salts incline to the formation of negative aluminate complexes, in addition to the positive ones. This tendency increases with increasing dilution, so that certain aluminium hydroxide sols stand at the boundary between positive and negative colloids. The occurrence of negative besides positive colloid complexes appears indeed to be a general phenomenon in metal oxide sols. We have proved it with certainty in the case of zirconium hydroxide sol, and made it very probable even in dilute ferric hydroxide sol. Thus a steady transition shows itself to the negative oxide sols.

The negative oxides also form colloid particles in accordance with the scheme shown for the positive oxide sols. Thus stannic acid—as suggested already by Zsigmondy—is peptized by alkali, through the agency of stannate ion, into colloidal stannic acid, which may be represented as

$$x(SnO\ )\ y\ \overset{--}{SnO_3}\ |\ \overset{++}{K_2}$$

in complete analogy with ferric hydroxide sol.

The sols of the noble metals, *e.g.* the much-investigated gold sols, are to-day considered as minute particles of pure gold, which receive their charge by emitting gold ions into the solution. This view causes difficulties in answering even quite elementary questions. Why do the particles not aggregate further until complete precipitation takes place? How is it that the gold is precipitated on continued dialysis, since, if the above view holds good, it cannot lose its charge in this way? How is it possible to prevent the floculation of gold sol during dialysis by the addition of a little ammonia to the external water, just as it can be prevented in the case of negative oxide sols by a little alkali, and of positive ones by traces of acid? Why is it impossible to prepare sols of the noble metals by electric dispersion in very clean vessels, *e.g.* of platinum, without the addition of alkali? Why cannot colloidal gold be amalgamated? Why does even the most energetic mechanical dispersion of pure mercury, according to Nordlund, not lead to sol formation?

All these and many other questions admit of unforced and satisfactory answers if we assume colloidal gold to be built up, not from particles of the pure metal, but from colloidal complex ions, in which the metallic particles receive their charge from a negative ion. Which is now the ionogenic molecule which furnishes these negative ions?

To answer this question we shall do well to examine, say, the preparation of gold sol according to Zsigmondy's method. It has been shown by Naumoff that the $AuCl_4$ first reacts with the K_2CO_3 present, with the formation of potassium aurate, KO_2Au, which we can consider as the salt of the auric acid, $Au^{III}.O.OH$. We have indeed satisfied ourselves that pure potassium aurate can be immediately reduced to red colloidal gold, *e.g.* by tannin, sugar, formaldehyde, and that even without any addition it is partly transformed into colloidal gold after a time. The reduction would have to proceed from the auri-compound *viâ* the auro-compound to pure gold. In this way, beside metallic gold, a mixed aurate of ter- and univalent gold is formed, to which our experience entitles us to

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ascribe the magnificent red colour. Such a mixed compound has been prepared a long time ago, and that by no less a person than Berzelius. Berzelius found on analysing the purple of Cassius that the gold was present therein as Au_2O_2, which he considered to be an auro-auric oxide. The mixture of $Au_2^{I}O_3$ and $Au_2^{III}O$ indeed gives $2(Au_2O_2)$.

We will call these or analogous aurate mixtures "porphyrate complexes," and ascribe to colloidal gold a structure quite analogous to that of negative stannic acid and consisting of a series of gold particles to which are attached porphyrate ions, *e.g.* one of potassium porphyrate.

Viewed in this way, the contrast between Berzelius's strictly chemical and Zsigmondy's colloidal conception of the purple of Cassius disappears entirely. Berzelius prepared his purple directly from gold and tin salts; Zsigmondy was able to produce it from colloidal gold and colloidal stannic acid. In the second case analysis will show varying ratios of gold and stannic acid, whereas in the first case stoichiometric ratios may result.

Although the study of sols of the noble metals is still incomplete in many details, we wish to point out that the new conception leads to simple answers to the questions put above, and that it explains the colour of colloidal gold as absorption colour, and the colour change as due to a coating of the particles with the aurous oxide (purple to indigo), which has to be removed by rubbing to expose the metallic surface. We may therefore say generally that in sol formation the aggregation of the insoluble neutral particles does not proceed as far as precipitation, but that, while the particles are still small, the addition of an ionogenic molecule leads to the formation of a stable, ionized complex. In this process a certain relation between the molecules appears essential, which rests in the mentioned examples on the identity of the central atom.

The formation of colloidal salts of the alkalies and alkaline in media having a dielectric constant lower than that of water proceeds in an analogous manner. Here, on the one hand, association of the neutral molecules takes place (P. Walden), while, on the other, the small residue of ionizing molecules produces the charge. In the organic colloids matters are also similar. In albumin the chemically joined amino-acids represent a chain of neutral particles, which receives its charge from one of the ionizing amino-acids. Starch consists of a chain of amyloses, the ion causing the charge being probably that of amylophosphoric acid (M. Samec). Similar, the resin acid ion in certain resins, and the fatty acid ion in soaps, as suggested by McBain, may be considered as the charged portion of the colloid complex.

We venture to hope that the views set forth above have the advantage of leading to a more rigid uniformity in colloid chemistry and of establishing it more firmly between the modern physics of crystals, on the one hand, and the chemistry of complex salts, on the other.

Laboratory for Physico-Chemical Biology
of the University of Vienna.

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SECTION I.—EMULSIONS AND EMULSIFICATION

Professor F. G. Donnan, C.B.E., F.R.S., opened the discussion in this section of the subject. The following is an abstract of his address :—

Emulsions may be defined as systems in which one liquid is dispersed in a second liquid in the form of small globules.

Dilute emulsions can be prepared by long-continued shaking of a pure hydro-carbon oil with pure water in a silica vessel. These emulsions often possess a high degree of stability, which must be ascribed to the influence of an electric double layer in preventing or hindering coalescence. Such emulsions possess all the characteristic properties of suspension colloids, though on a rougher scale. Investigations have shown that the interfacial potential difference and the corresponding stability of the emulsion are affected by positive and negative ions and by oppositely charged colloids in just the same manner as correspondingly charged suspension colloids.

Emulsification is greatly aided by the presence of a third substance, which forms a protecting film or membrane round the globules of the dispersed fluid. Such substances must always be used if it is desired to prepare emulsions of any considerable degree of concentration. Substances which lower the interfacial tension and therefore tend to concentrate at or in the interfacial layer, as, for example, the soaps, act as efficient emulsifiers. Many colloidal substances, such as gums, gelatine, etc., act as emulsifiers, and are largely used for this purpose in practical life.

Pickering has employed basic salts of copper, iron, etc., as emulsifying agents, and even such things as soot and lampblack have been successfully employed for this purpose in certain cases. The phenomena of interfacial adsorption and concentration, with the resulting formation of protecting films or membranes, play therefore a very important role in the formation and stabilisation of most emulsions, though the effects due to the electrical double layer and the differential adsorption of ions cannot be neglected.

It was thought at one time that the close packing of equal spheres would impose an upper limit to the amount of one liquid which could be emulsified in another. But this has been shown by later work not to be the case.

Very interesting phenomena occur when an emulsion "inverts," *i.e.*, when on the further addition of the dispersed liquid the latter exchanges its role with the liquid which has previously played the part of the continuous medium. This sudden change of type can be very readily detected by the sudden change of electrical resistance. When dealing with hydrocarbon and fatty oils emulsified in water by means of soaps, investigation has shown that electrolytes play an important part in determining the position of the inversion point and the nature of the liquid which forms the continuous medium. Thus di- and trivalent cations tend to render the oil the continuous phase, whilst univalent cations, and especially the alkali hydroxides, tend to cause the oil to be dispersed in a continuous aqueous phase. The physical factors which determine these phenomena are not yet completely elucidated.

The study of emulsions has thrown much light on the phenomena exhibited by colloidal systems, though the very much larger size of

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the dispersed particles, and the correspondingly diminished Brownian motion in the case of even the finest emulsions, differentiate them in many important respects from colloidal solutions.

BIBLIOGRAPHY OF EMULSIONS

Author.	Title of the Contribution.	Reference.
E. Mach	Ueber Flüssigkeiten welche suspendirte Körperchen enthalten.	*Pogg. Ann.*, **126**, 329, 1865.
W. Kühne	Chapter on Emulsions	*Lehrbuch der Physiol. Chem.*, 129, 1866
J. Plateau	Experimentelle und theoretische Untersuchung über die Gleichgewichts Figuren einer flüssigen Masse ohne Schwere.	*Mém. d. Brux.*, **37**, 3, 1868. *Pogg. Ann.*, **141**, 44, 1870.
E. Donath	The Testing of Bees' Wax for Adulterations.	*J. C. S.*, **26**, 194, 1873.
L. Schischkoff	Chemical Composition of Milk	*Ber.* **12**, 1490–92; also *J. C. S.*, **38**, 273, 1880.
John Gad	Zur Lehre von der Fettabsorption	*Arch. Anat. Physiol.*, 181, 1878.
G. Quincke	Ueber die physikalischen Eigenschaften dünner fester Lamellen	*Wied. Ann.*, **35**, 562, 1888.
	Ueber Periodische Ausbreitungen Flüssigkeitsoberflächen und dadurch hervorgerufene Bewegungserscheinungen.	*Wied. Ann.*, **35**, 580, 1888.
B K. Rachford	The Influence of Bile on the Fat-splitting Properties of Pancreatic Juice.	*Journ. Physiol.*, **12**, 72, 1891.
B. Moore & D. P. Rockwood.	On the Mode of Absorption of Fats	*Journ. Physiol.*, **21**, 74, 1897.
B. Moore & C. J. I. Krumbholz.	On the Relative Power of various forms of Proteid in Conserving Emulsions.	*Proc. Physiol. Soc. Lond.*, 54, 1898.
F. G. Donnan	Ueber die Natur der Seifenemulsionen.	*Zeit. Physikal. Chem.*, **31**, 42, 1899.
Agnes Pockels	Untersuchung von Grenzflächenspannungen mit der Cohäsionswaage.	*Wied. Ann.*, **67**, 668, 1899.
Lord Rayleigh	Investigations in Capillarity: The size of Drops—The Liberation of Gas from Supersaturated Solutions—Colliding jets—The Tension of contaminated water-surfaces.	*Phil. Mag.*, (5), **48**, 321, 1899.
J. Von Zawidski	Zur Kenntnis der Zusammensetzung der Oberflächenschichten wässeriger Lösungen.	*Zeit. Physikal. Chem.*, **35**, 77, 1900.
Clara Benson	The Composition of the Surface Layers of Aqueous Amyl Alcohol.	*Journ. Phys. Chem.*, **7**, 532, 1903.
W. Ramsden	Separation of Solids in the Surface Layers of Solutions and Suspensions (Observations on Surface Membranes, Bubbles, Emulsions and Mechanical Coagulation).	*Proc. Roy. Soc.*, **72**, 156, 1903.
H. W. Hillyer	On the Cleansing Power of Soap	*Journ. Amer. Chem. Soc.*, **25**, 511, 1903.
W. Ramsden	Abscheidung fester Körper in den Oberflächenschichten von Lösungen und Suspensionen (Beobachtungen über Blasen, Emulsionen und mechanische Koagulation).	*Zeit. Physikal Chem.*, **47**, 336, 1904.

Digitized by Google

Author.	Title of the Contribution.	Reference.
K. Beck	Beiträge zur Bestimmung der inneren Reibung.	*Zeit. Phys. Chem.*, **58**, 409, 1907.
S. U. Pickering	Emulsions	*J. C. S.*, **91**, 2002, 1907.
S. R. Milner	On Surface Concentration and the Formation of Liquid Films.	*Phil. Mag.*, (6) **13**, 96, 1907.
	Grösse und Elektrische Ladung der Oelteilchen in Oel-Wasser-Emulsionen.	*Koll. Zeit.*, **4**, 211, 1909.
W. C. McC. Lewis	Die Oberflächenspannung Kolloider und Emulsoider Partikel und ihre Abhängigkeit von der Grenzgrösse der Letzteren.	*Koll. Zeit.*, **5**, 91, 1909.
F. G. Donnan & H. E. Potts.	Ueber die Emulsierung von Kohlenwasserstoffölen durch wässerige Lösungen fettsaurer Salze. Ein Beitrag zur physikalischchemischen Theorie der Seifen-Emulsionen.	*Koll. Zeit.*, **7**, 208, 1910.
S. U. Pickering	Ueber Emulsionen	*Koll. Zeit.*, **7**, 11, 1910.
W. C. McLewis	Die Adsorption in ihrer Beziehung zur Gibbschen Theorie. Dritte Abhandlung: Die Adsorbirende Quecksilber Oberfläche.	*Zeit. Phys. Chem.*, **73**, 129, 1910.
E. Hatschek	The Direct separation of Emulsions by Filtration and Ultrafiltration.	*J. Soc. Chem. Ind.*, **29**, No. 3, 125, 1910.
E. Hatschek	Die Filtration von Emulsionen und die Deformation von Emulsionsteilchen unter Druck.	*Koll. Zeit.*, **7**, 81, 1910.
Wa Ostwald	Beiträge zur Kenntnis der Emulsionen.	*Zeit. Koll. Chem.*, **6**, 103, 1910.
	Der Kritische Punkt bei Emulsionen.	*Zeit. Koll. Chem.*, **7**, 64, 1910.
T. Brailsford Robertson.	Notiz über einige Faktoren welche die Bestandteile von Oel-Wasser-Emulsionen bestimmen.	*Koll. Zeit.*, **7**, 7, 1910.
F. G. Donnan & J. T. Barker.	An Experimental Investigation of Gibbs's Thermo-dynamical Theory of Interfacial concentration in the case of an Air-water Interface.	*Proc. Roy. Soc.*, **85** (A), 557, 1911.
E. Hatschek	Die Beständigkeit von Oel-Wasser Emulsionen.	*Koll. Zeit.*, **9**, 159, 1911.
E. Groschuff	Ueber die Beständigkeit von Wasseremulsionen in Kohlen-Wasserstoffölen.	*Koll. Zeit.*, **9**, 257, 1911.
Höber	Book	*Phys. Chem. der Zelle und der Gewebe*, 3rd Edition, 293, 1911.
Ridsdale Ellis	Die Eigenschaften der Oelemulsionen. I. Die Elektrische Ladung.	*Zeit. Phys. Chem.*, **78**, 321, 1912.
Ridsdale Ellis	Die Eigenschaften von Oelemulsionen. II. Beständigkeit und Grösse der Kügelchen.	*Zeit. Phys. Chem.*, **80**, 597, 1912.
Ridsdale Ellis	A Neutral Oil Emulsion as a Model of a Suspension Colloid.	*Trans. Faraday Soc.*, Vol. **9**, 14, 1913.
W. D. Bancroft	The Theory of Emulsification I.	*Journ. Phys. Chem.*, **16**, 177, 1912.
	,, ,, ,, ,, II.	*Journ. Phys. Chem.*, **16**, 345, 1912

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Author.	Title of the Contribution.	Reference.
W. D. Bancroft	The Theory of Emulsification III.	*Journ. Phys. Chem.*, **16**, 475, 1912.
	" " " " IV.	*Journ. Phys. Chem.*, **16**, 739, 1912.
	" " " " V.	*Journ. Phys. Chem.*, **17**, 501, 1913.
	" " " " VI.	*Journ. Phys. Chem.*, **19**, 275, 1915.
	" " " " VII.	*Journ. Phys. Chem.*, **19**, 513, 1915.
	" " " " VIII.	*Journ. Phys. Chem.*, **20**, 1, 1916. *Trans. Electrochem. Soc.*, **23**, 294, 1913.
Emil Hatschek	The General Theory of Viscosity of Two-Phase Systems.	*Trans. Faraday Soc.*, **9**, 34, 1913.
W. A. Patrick	Adsorption at a Water-mercury Interface.	*Zeit. Phys. Chem.*, **85**, 545, 1914.
G. H. A. Clowes	Action of Antagonistic Electrolytes on Emulsions and Living Cells.	*Proc. Soc. for Exp. Biol. and Med.*, **11**, 1, 1913.
T. R. Briggs	The Electrochemical Production of Colloidal Copper.	*Journ. Phys. Chem.*, **17**, 296, 1913.
Frank Powis	Der Einfluss von Elektrolyten auf die Potentialdifferenz an der Oel-Wasser Grenzfläche einer Oelemulsion und an einer Glas-Wassergrenzfläche.	*Zeit. Phys. Chem.*, **89**, 91, 1914.
Frank Powis	Der Einfluss der Zeit auf die Potentialdifferenz an der Oberfläche von in wässerigen Lösungen suspendierten Oelteilchen. II.	*Zeit. Phys. Chem.*, **89**, 179, 1914.
F. R. Newman	Experiments on Emulsions	*Journ. Phys. Chem.*, **18**, 34, 1914.
Frank Powis	Die Beziehung zwischen der Beständigkeit einer Oelemulsion und der Potentialdifferenz an der Oel-Wassergrenzfläche, und die Koalgulation Kolloider Suspensionen.	*Zeit. Phys. Chem.*, **89**, 186, 1914.
T. R. Briggs	Experiments on Emulsions: Adsorption of Soap in the Benzene-water Interface.	*Journ. Phys. Chem.*, **19**, 210, 1915.
T. R. Briggs & H. F. Schmidt.	Experiments on Emulsions II.	*Journ. Phys. Chem.*, **19**, 479, 1915.
G. H. A. Clowes	Protoplasmic Equilibrium	*Journ. Phys. Chem.*, **20**, 407, 1916.
S. A. Shorter & S. Ellingworth	On the Emulsifying Action of Soap—A Contribution to the Theory of Detergent Action.	*Proc. Roy. Soc.*, **92** (A), 231, 1916.
H. W. Gillet	Emulsions and Suspensions with Molten Metals.	*Journ. Phys. Chem.*, **20**, 729, 1916.
M. H. Fischer and Marion O. Horker	Formation and Decay of Emulsions	*Koll. Zeit.*, **18**, 129, 1916.
	Ueber die Analogie des Verhaltens von Emulsionen und des Verhaltens von Fett im Protoplasm.	*Koll. Zeit.*
M. H. Fischer	Theory of Emulsions	*Science*, **43**, 468, 1916.
L. Roon & R. E. Oesper.	A Contribution to the Theory of Emulsification based on Pharmaceutical Practice.	*J. Ind. Eng. Chem.*, **9**, 156, 1917.
I. C. Hall	The Stability of Emulsions in the constricted Tube and Marble Device for Anærobiosis.	*Journ. Phys. Chem.*, **21**, 609, 1917.

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Author.	Title of the Contribution	Reference.
A. U. Schlaepfer	Water-in-Oil Emulsions	*J. C. S.*, **113**, 522, 1918.
V. Lehner & G. M. Bishop.	Some Studies of Soap Solutions II.	*Journ. Phys. Chem.*, **22**, 68, 1918.
	,, ,, ,, ,, III.	*Journ. Phys. Chem.*, **22**, 95, 1918.
W. P. Davey	Emulsion: A New Method for making Emulsions. (*b*) Properties of Emulsions.	*Phys. Review*, **11**, 138, 1918.
S. E. Sheppard	Emulsification at an Oil-water Interface.	*Journ. Phys. Chem.*, **23**, 634, 1919.
W. C. Moore	Emulsification of Water and Ammonium Chloride Solutions by means of Lamp-black	*J. Amer. Chem. Soc.*, **41**, 940, 1919.
W. Clayton	The Modern Conception of Emulsions.	*J. Soc. Chem. Ind.*, **38**, 113, T, 1919.
S. S. Bhatnagar	Studies in Emulsions, Part I.: A New Method of Determining the Inversion of Phases.	*J. C. S.*, **117**, 542, 1920.
T. R. Briggs	Experiments on Emulsions III.	*Journ. Phys. Chem.*, **24**, 20, 1920.
S. S. Bhatnagar & W. E. Garner.	The effect of the Addition of Certain Fatty Acids on the Interfacial Tension between B.P. Paraffin Oil and Mercury.	*Journ. Soc. Chem.*, **39**, No. 13, 185, 1920.
T. R. Briggs, F. R. Du Casse & L. R. Clarke.	Experiments on Emulsions IV.	*Journ. Phys. Chem.*, **24**, 147, 1920.
M. G. White & J. W. Marden.	The Surface Tension of certain Soap Solutions and their Emulsifying Powers.	*Journ. Phys. Chem.*, **24**, 617, 1920.
S. S. Bhatnagar	Precipitation of Suspensoids and Reversal of Phases in Emulsions by Electrolytes: an Analogy.	*Symposium on Colloids, Faraday Soc.*, Octr., 1920.
A. W. Thomas	A Review of the Literature of Emulsions.	*J. Ind. Eng. Chem.*, **12**, 177, 1920.
H. N. Holmes & Wm. C. Child.	Gelatine as an Emulsifying Agent	*Journ. Amer. Chem. Soc.*, **42**, 2049, 1920.
W. Clayton	Report on Emulsions	*Brit. Assoc. Colloid Reports*, **2**, 114, 1918.
S. S. Bhatnagar	Studies in Emulsions, Part II.: The Reversal of Phases by Electrolytes and the Effects of Free Fatty Acids and Alkalies on Emulsion Equilibrium.	*J. C. S.*, **119**, 61, 1921.
S. S. Bhatnagar	Studies in Emulsions, Part III.: Further Investigations on the Reversal of Type by Electrolytes.	*Communicated J. C. S.*, 1921.
	Studies in Emulsions, Part IV.: Solubilities of some Mono-, Bi- and Trivalent Soaps in Paraffin Oil and Benzene and their Effects on the Interfacial Tension between the Organic Solvents and Water.	
H. Bechhold, L. Dede & L. Renier.	Dreiphasige Emulsionen	*Koll. Zeit.*, **28**, 6, 1921.

BOOKS.

Colloids in Biology and Medicine, by H Bechhold, 1919.
Margarine, by W. Clayton, 1921.
(Longman, Green & Co.).
Kapillarchemie, by H. Freundlich, 1920.
Applied Colloid Chemistry, by W. D. Bancroft, 1921.

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EMULSION PROBLEMS IN MARGARINE MANUFACTURE

BY

WILLIAM CLAYTON, M.Sc.

Margarine is a substitute for butter, certain animal and vegetable oils and fats replacing butterfat. The oils and fats are liquefied together in certain proportions depending on the quality of the margarine required, and then churned with soured milk to form an emulsion. This emulsion is rapidly cooled, either by means of a spray of ice-cold water under pressure, or by flowing on to well-cooled revolving drums. The product in each case is then worked up by suitable kneading machinery to the required butter consistency and texture.

Margarine manufacture offers a splendid field for colloid research in several directions, but particularly in emulsions, both liquid and solid. Practically no published work appears on solid emulsions like butter and margarine, and as regards liquid emulsions, practice in margarine manufacture has followed empirical rules rather than definite physico-chemical conclusions.

The present discussion may conveniently include three main points in the making of a margarine emulsion :—

(*a*) Factors depending on the degree and mode of agitation employed in mixing.

(*b*) Factors depending on the animal and vegetable oils and fats used.

(*c*) Factors depending on the water, milk, and other ingredients employed.

(*a*) Factors depending on the Degree and Mode of Agitation employed in Mixing

The most essential factor in the production of a margarine of a butter-like texture, is the preparation of a stable and *suitably-phased* emulsion[1] containing from 77 per cent. to 84 per cent. fat and 23 per cent. to 16 per cent. water (milk serum). The milk used is at a temperature of about 7° C., and the melted mixture of oils and fats at about 40° C. Before actually chilling the emulsion its temperature is reduced to about 24° C., so that a thick custard-like emulsion ensues, of greatly enhanced stability. This greater stability is due to the viscosity of the system, and furnishes an instance where viscosity is desirable in emulsion preparation.[2] The object of chilling the emulsion is to fix the fine-grained condition arrived at, whereby the desirable intimate and finely-divided mixture is maintained in the solid state. Any " breaking " of the emulsion would lead to the formation of unemulsified fat, whereby the texture of the final product would be unsatisfactory.

Two types of emulsifying machines are in common use in margarine manufacture. The first is essentially a jacketed tank, permitting temperature control by circulating either hot or cold water. Milk is admitted to the tank, and then the oil mixture slowly run in, whilst constant agitation is maintained, *e.g.*, by means of rapidly-revolving baffle plates.

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It is absolutely essential to run the oils into the milk, and not *vice-versa*.[3] Thus a fine-grained emulsion results, of the oil-in-water type, which on cooling to 24° C. (with constant agitation) becomes remarkably permanent. The more slowly the oil is run in, the better the results obtained.

If on the other hand the oils be in the churn in bulk and the milk run in, an emulsion of the water-in-oil type ensues. The same thing happens if both phases are placed in bulk in the churn (say 80 per cent. oil and 20 per cent. milk) without undue mixing, and then the agitating device set in motion. On consideration of volume factors alone, it will be evident that if one has the oil phase in bulk and milk is introduced, stirring continually, the conditions from the purely mechanical aspect of disintegration of particles favour the formation of the water-in-oil type of emulsion. Such an emulsion is not "permanent." As soon as the agitation ceases, separation into layers occur, owing to the fact that the very nature of the emulsifying agents present, viz., milk colloids, demands the oppositely-phased system. Of course, this water-in-oil type emulsion can be "fixed" by any of the methods of rapid chilling used in margarine manufacture, but even then, the solid emulsion produced is far from satisfactory in the subsequent processes, and may well lead to a final margarine of poor texture.

The second type of emulsifying machine aims at the *continuous* production of emulsions, whereby there is economy in space, time, and power. The principle underlying continuous churns is the simultaneous admission of the oils and milk into a thermo-regulated chamber, whence, after some suitable device has ensured intimate mixing, an emulsion is discharged in a continuous stream.[4] It is at once apparent that the same degree of freedom of the control of physical or mechanical factors is not permitted with this churn as with the older tank type. In my experience, even when using milk and oils, *i.e.*, when the purely *physico-chemical* conditions are satisfied, different *mechanical* treatments may lead to either the oil-in-water or water-in-oil type of emulsion. Sometimes, the passage through a continuous churn (wherein blades revolving 1,500 r.p.m. cause violent agitation) of a margarine emulsion of the oil-in-water type, will completely reverse the type of emulsion. Probably volume factors exercise a marked influence in such inversions.

It may be noted here that the nature of a margarine solid emulsion can be determined by staining with Sudan and examining under the microscope,[5] or by extending Briggs'[6] drop-method of dilution, by placing a small piece of the margarine in cottonseed oil at 15° C.; if the margarine is of the water-in-oil type, it slowly dissolves, if of the opposite type, it is unaffected. An electrical method was proposed by the author,[7] based on the idea that though a small conductivity may result in an emulsion of the oil-in-water type, practically no conductivity would be observed in the case of a water-in-oil emulsion. That such a scheme is practicable has recently been shown by Sherrick[8] and by Bhatnagar.[9]

The effects of different methods of agitation, and the degree of any one kind, on a mixture of oil and an aqueous phase, deserve far more attention than hitherto given. Undoubtedly one can both make and "break" an emulsion by agitation. Thus Sheppard,[10] working on the emulsification of nitrobenzene in sulphuric acid, found that "de-emulsification was accelerated by slow shaking or even single vibration in some cases, for emulsions which remained stable

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at rest, while shaking gently at a slightly higher frequency would re-emulsify to a system again stable at rest." The influence of vibration on emulsions has been noted by Ayres,[11] and he mentions an instance where an emulsion, so stable as to defy separation in a centrifuge, was de-emulsified by the vibration attendant upon its transport in an express railway train.

The prevalent idea regarding emulsification in general, and margarine churning in particular, is to agitate the mixture of milk and oils as violently as possible. Such agitation, it has been argued, results in the formation of very small globules, a most desirable feature in a stable emulsion. Consequently an empirical limit only is set on the degree of stirring up an emulsion. For any given type of emulsifying machine, it seems reasonable to believe that an optimum degree of agitation is possible, favouring a very stable system.

Shaking is an inferior method of making emulsions, because as the emulsion becomes more perfect, the smashing action between the relatively heavy and light particles becomes more feeble, whereas the smashing forces should be increased. Briggs[12] has recently shown that "intermittent shaking was vastly more effective than uninterrupted agitation," and that "intermittent shaking may be six hundred or even a thousand times more effective than uninterrupted but equally violent agitation." From his results, it would appear that the ideal process of emulsification is one wherein the dispersed phase is as completely disintegrated as possible, whilst the continuous medium is left as far as possible unbroken. It seems to me that continuous shaking would give equally as good results as the intermittent shaking, provided the emulsified portions of the mixture are continually removed from the mass so that the energy of shaking is concentrated on the remainder.

(*b*) Factors depending on the Animal and Vegetable Oils and Fats used

The solid fats used in margarine manufacture include stearine (M.Pt. = 50° C.), beef-jus (48° C.), oleo (30° C.), lard (33° C.), palm-kernel oil (28° C.), and coconut oil (25° C.), whilst the liquid oils include cottonseed, arachis, soya, rape, sesame, etc. A margarine mixture may include from three to six of these ingredients, so proportioned as to give a melting-point of about 26° C.[13]

Experiments have been made to inquire whether these various ingredients were alike in their capacity of being emulsified, or whether by a suitable choice of oils and fats, a margarine mixture could be obtained which would with greater ease give an emulsion of more than the usual stability. Using the Donnan drop-pipette, numerous drop number determinations were made of various oils and fats against water at various temperatures.

The first point observed was the fact that only a small difference in drop numbers exists for these oils and fats, *e.g.*, at 35° C. against pure water, the following numbers were repeatedly observed :—

Palm kernel oil	= 74	lard	= 59
butterfat	= 71	oleo	= 66
cottonseed oil	= 65	arachis oil	= 66
coconut oil	= 61	soya bean oil	= 68

The effect of the free-fatty acids in edible oils is small. Thus no change in drop number was given by various samples of the liquid oils, with free fatty acid contents ranging from 0·05 per cent. (as

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oleic acid) to 0·5 per cent., the figures usually found. The coconut oils and palm-kernel oils investigated had free fatty acid contents of 0·05 per cent. to 0·08 per cent. (as lauric acid). A coconut oil not so well refined as the usual edible oil employed in margarine, and possessing a distinct odour of coconut, had 1·85 per cent. of free lauric acid, and the drop number at 35° C. was 73 instead of the usual figure 61.

Temperature has no pronounced influence on the interfacial tension, an observation agreeing with the results of Meunier and Maury,[14] though they used oils very different to mine.

Effect of Temperature on Drop Number

Arachis Oil-water.	Cottonseed Oil-water.	Coconut Oil-water.
25·5° C. = 66 drops.	27·5° C. = 65.	30° C. = 69.
46·0° C. = 65 drops.	35·0° C. = 65.	35·0 = 61.
50·0° C. = 64·5 drops.	50·0° C. = 63.	50·0 = 65.

Palm Kernel Oil-water.	Soya Bean Oil-water.	Lard-water.	Oleo-water.
30° C. = 73	35° C. = 68	35° C. = 59	35° C. = 66
35° C. = 74	50° C. = 68·5	50° C. = 66	50° C. = 69
50° C. = 61			

Tap water gave results practically identical with distilled water.

(c) Factors depending on the Water, Milk, and other Ingredients employed

It is the practice to add salt to margarine during the final stage of blending. In the use of the author's invention,[15] of a machine for the continuous production of margarine, the salt is added in solution in the milk during emulsification. Drop number determinations have shown that NaCl promotes the dispersion of oils and fats in water. For example, at 35° C :—

Coconut Oil in :		Butterfat in :	
Water	= 61 drops.	Water	= 71 drops.
1 per cent. NaCl	= 65·5 ,,	1 per cent. NaCl	= 80 ,,
2 ,, ,,	= 70 ,,	2 ,, ,,	= 84·5 ,,
3 ,, ,,	= 74 ,,	3 ,, ,,	= 87·5 ,,

At 13 per cent. NaCl concentration (the concentration of the salt present in the aqueous phase of the total emulsion) no drop numbers were determined, because of sausage-like formations of the drops.

The explanation as to why NaCl, which will " break " emulsions of oil in (say) soap solution, facilitates dispersion in pure water, seems to be that by preferential adsorption of the Cl ion at the oil-water interface, caustic soda is formed which unites with the free fatty acids present in the oil, and so forms a soap. Thus two coconut oils were examined at 35° C. One had 0·07 per cent. free fatty acid, the other 1·85 per cent. In a 1 per cent. NaCl solution they gave drop numbers of 65·5 and 79 respectively. Actual tests on a works scale have shown that salt (2 per cent. concentration on the total margarine, 13 per cent. concentration in the aqueous phase) does facilitate emulsification.

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Emulsifying agents are frequently added to the milk or oil in margarine manufacture, and numerous patents for such additions exist, *e.g.*, egg-yolk, lecithin, gelatin, glycerin, albumin, etc. Gelatin is an excellent emulsifier. A palm kernel oil giving a drop number of 73 in water in 30° C. gave 120 drops in 1 per cent. gelatine. Two samples of oils at 25° C. gave the following results :—

Cottonseed Oil in :		Arachis Oil in :	
Water - - -	66 drops.	Water - - -	66 drops.
0·25 per cent. gelatine	124 „	0·5 per cent. gelatine	140 „
0·50 „ „	137 „	1·0 „ „	148 „
1·0 „ „	143 „	2·0 „ „	155 „
2·0 „ „	149 „	3·0 „ „	163 „
3·0 „ „	149·5 „		
4·0 „ „	150·0 „		

The curve given by plotting the results for cottonseed oil suggests a maximum effect at about 3 per cent., but this question demands further inquiry.[16]

It is now evident that extensive investigations require to be made before a thorough account of a margarine emulsion is complete. It is probably the most complex emulsion system in industrial practice. The oils and fats are not emulsified with water only (except in special cases, *e.g.*, " pastry margarines ") but with milk, and this milk has been artificially soured by the action of lactic acid bacterial. In the milk there is lactic acid, milk colloids, lactose and solid clots of casein. What the effects of these substances are on the emulsion is a field for further research.

Preliminary measurements indicate that lactic acid has a slight positive dispersing effect and lactose a more pronounced effect. Thus a coconut oil giving a drop number of 69 in water at 30° C. gave a drop number of 116 in 1 per cent. lactose. In three separate solutions of lactose, coconut oil gave 116, 118 and 116 drops. Such a result is quite unexpected, and is receiving further investigation.

In conclusion, I take this opportunity of thanking Calder's Margarine Co., Ltd. (Liverpool), for affording me every facility to carry out these experiments.

Bibliography

[1] *Vide* Clayton : " Theory of Emulsions and Margarine Churning," *Margarine Journal*, **2**, 13, 503–4, 1920.
[2] Hillyer, *J. Amer. Chem. Soc.*, **25**, 513, 1903.
[3] *Vide* Blichfeldt, Eng. Pat. 4505, 1912.
[4] Well-known types of continuous churns : Schröder, *Eng. Pat.* 25404, 1905 ; *Germ. Pat.* 309717, 1917; Risberg, *Eng. Pat.* 25890, 1907; Silkeborg, *Eng. Pat.* 4657, 1914; Blichfeldt, *Eng. Pat.* 18048, 1914; Leitch, *U.S. Pat.* 1266501, 1918.
[5] Robertson, *Koll. Zeits.*, **7**, 7–10, 1910.
[6] Briggs, *J. Phys. Chem.*, **19**, 478–99, 1915.
[7] Clayton, *Brit. Assoc. Colloid Reports*, 2, 114, 1918; *J.S.C.I.*, **38**, 113–118T, 1919.
[8] *J. Ind. Eng. Chem.*, **12**, 135, 1920.
[9] *Journ. Chem. Soc.*, 1920, pp. 542–552.
[10] *J. Phys. Chem.*, **23**, 634–9, 1919.
[11] *J.S.C.I.*, **35**, 678, 1916.
[12] *J. Phys. Chem.*, **24**, 120–6, 1920.
[13] *Vide* Clayton, " *Margarine* " (Longmans), 1920, p. 36.
[14] *Collegium*, 1910, 277–84, 285–87.
[15] Clayton and Nodder, *Eng. Pat.* 147257, 1920.
[16] *c.f.* Holmes and Child, *J. Amer. Chem. Soc.*, **42**, 2053, 1920.

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REVERSAL OF PHASES IN EMULSIONS AND PRECIPITATION OF SUSPENSOIDS BY ELECTROLYTES : AN ANALOGY

BY

SHANTI SWARUPA BHATNAGAR

Donnan pointed out the resemblance between emulsions and colloidal solutions as early as 1899 (cf. *Zeit. Phys. Chem.* **31,** 42, 1899). Further work carried out by Ellis (*Zeit. Phys. Chem.*, **78,** 321, 1911) and by Lewis (*Zeit. Kolloid Chem.*, **4,** 211, 1909) has established that neutral oil emulsions behave like model suspension colloids. The investigations of Hatschek on the influence of electrolytes on emulsions, in which the disperse phase and the continuous medium were of equal densities (*Zeit. Kolloid*, **9,** 159, 1911), pointed out the resemblance still further. It was, however, found that neutral oil emulsions were not particularly sensitive to the effect of electrolytes.

There has been some hesitation on the part of various investigators on emulsions in advocating the study of the effects of electrolytes on soap emulsions because they are not free from electrolytes. As far as the author is aware, the only work in this field is a paper by Clowes (*J. Physical Chem.*, **20,** 445, 1916). His work is, however, restricted to a particular type of emulsion only, and the accuracy of the quantitative data obtained by him is, in his own words, "rough at best," because of the difficulties in determining accurately and sharply the point when an emulsion of oil-in-water changes into one of water-in-oil under the influence of electrolytes.

There are two methods generally in use to determine the type of the emulsion, namely, the "colour-indicator" method of Robertson and the drop-method of Briggs. In the colour-indicator method of Robertson, use is made of some oil soluble dye like Sudan III. In an emulsion of oil-in-water, this colour remains confined to the particles of oil which exist as globules, but in an emulsion of water-in-oil the colour spreads over the whole surface of the continuous phase and the microscopical examination reveals the type of the emulsion under consideration.

This method has been found unsatisfactory by Newman (*Z. Physikal. Chem.*, **18,** 34, 1914), and it is also likely that the character and stability of an emulsion might be disturbed by the introduction into the system of a foreign substance like Sudan III., and thus vitiate the accuracy of the quantitative data. That such doubts are justified is abundantly clear from the observations of Clowes (*J. Physical Chem.*, **20,** 445, 1916), who finds that organic impurities have an appreciable effect on the size of globules in emulsions.

The drop-method of Briggs is based on the principle that an emulsion can be diluted by adding more of the continuous medium, but not by adding excess of the disperse phase. This method suffers a disadvantage on account of the fact that a single drop of an emulsion may not always represent the emulsion, whilst if a representative portion of an emulsion is shaken with a large quantity of oil or water, the temporary emulsion due to mere mechanical shaking may make it extremely difficult to determine the type.

Besides the defects pointed out above, these methods completely fail to give a sharp indication of the critical point, and are, therefore,

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not convenient for studying the effects of electrolytes and other substances on emulsions. In order to obtain a correct quantitative data on the effect of electrolytes on emulsions of soap solution and oil, an electrical method was employed which has been described in detail in a paper contributed by the author to the Chemical Society (*J.C.S.*, **117**, 542, 1920).

The principle of this method is based on the fact that an emulsion of oil-in-water type, specially when soap solutions are used, undergoes a sudden drop in electrical conductivity at the point when it changes into the reverse type under the influence of electrolytes.

The procedure of using alkaline solutions and free fatty acids in the oil employed by Clowes has been found unsatisfactory for repeating observations. When dilute solutions of alkalies are used, a comparatively large amount of free fatty acid in the system is left unneutralised. The presence of free fatty acid or alkali makes the system more complex. Besides, alkali and acids have been found to have definite effects on the degree of dispersion in emulsions. In order to obtain consistent and comparable results, various pure soap solutions were employed.

It is to be noted here that very special precautions have to be observed in ensuring identical conditions of shaking, form and size of the vessels, &c. used (cf. *J.C.S.*, **117**, 542, 1920). A large number of electrolytes was examined, and the detailed results obtained have been recently communicated in a paper to the Chemical Society. Two representative tables of results are shown below.

Experiments with Electrolytes

Volume of oil phase = 10 cc.
Volume of aqueous phase = 10 cc.
R = inversion point.

TABLE 1
(*Soap Potassium Oleate.*)

Amount of Soap, in millimols at R.	Barium Nitrate, in millimols at R.	$Ca(NO_3)_2$ in millimols at R.	Amount of $Pb(NO_3)_2$, in millimols at R.	$Cr_2(SO_4)_3$, in millimols at R.	$Al_2(SO_4)_3$, in millimols at R.
0·080	2 × 0·0199	2 × 0·020	2 × 0·0198	0·017	0·014
0·10	2 × 0·0251	2 × 0·027	2 × 0·0252	0·019	0·017
0·151	2 × 0·041	2 × 0·042	2 × 0·04	0·028	0·025
0·162	2 × 0·044	2 × 0·044	2 × 0·044	0·03	0·027

TABLE 2
(*Soap Sodium Stearate.*)

Amount of Soap, in millimols, at R.	$Ca(NO_3)_2$, in millimols at R.	$Al^3(SO_4)_3$, in millimols at R.	$Cr_2(SO_4)_3$, in millimols at R.	$Ba(NO_3)_2$	$Ca(NO_3)_2$	$Ph(NO_3)_2$
0·09	0·040	0·015	0·016	0·0398	0·040	0·0396
0·12	0·056	0·020	0·023	0·0502	0·054	3·0504
0·16	0·090	0·028	0·029	0·082	0·084	0·08
0·2	0·10	0·03	0·032	0·088	0·088	0·088

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TABLE 3

Data of As_2S_3 *sols by Mukherjee, J. Amer. Chem. Soc.*, **37**, 2030, 1915.

Lith. Chloride concentration.	Time for perceptible Change.	Alum. Sulph. concentration.	Time for perceptible Change.
N/10	7 minutes	N/2000	9 minutes.
N/9	5 minutes	N/10000	Less than a minute.
N/8	3 minutes	—	—
N/7	Few seconds	N/9000	Five seconds.
Barium chloride	—	—	—
N/700	15 minutes	—	—
N/600	Few seconds	—	—

TABLE 4

Order of precipitating Power of Cations for various Suspensoid Systems.

[1] Gold.—Al>Ba,Sr>Ca>Na>H>Cs>Rb>K>Na>Li
[2] Platinum.—Al,Pb>Ba>K>Na
[3] Copper Ferrocyanide.—Al>Ba>H>Cs>Rb>K>Na>Li
[4] Prussian Blue.—Fe,Cr,Al>Ba>H>Cs>Rb>K>Na>Li
[5] Silver.—Al>Ba,Sr,Ca>H>Cs>Rb>K>Na>Li

REFERENCES

[1] Galecki, *Zeitsch. Anorg. Chem.*, 1912, **74**, 174; Westgren, *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1–30 ("Chemistry of Colloids," by Taylor).
[2] Freundlich, *Kapillarchemie*, 1909, 352.
[3] and [4] Pappada, *Koll. Zeitsch.*, 1910, **6**, 83; 1911, **9**, 136.
[5] Pappada, *Gaz. Chim.*, 1912, **42**, I., 263.

The results shown in Tables 1, 2 indicate in a marked manner the differences in the amounts of various electrolytes required to bring about the reversal of phases. Tables 3 and 4 are the data obtained for precipitation of gold, arsenious sulphide, and other sols by electrolytes. The effect of the valency of the electrolyte is worth noting. In both cases the trivalent electrolytes have a greater effect than bivalent ones. The power of reversing the phases in these electrolytes is in the order Al>Cr>Nickel>Lead>Barium>Strontium and Ca. It is interesting to note that, in many suspensoid sols also, the same order persists under different conditions. The author has investigated various soaps, and although the amount of electrolytes required to bring about the reversal of phases differs with different soaps, the valency effect of the electrolyte and the order still holds good.

EFFECT OF DILUTION ON THE REVERSAL OF PHASES BY ELECTROLYTES

In order to examine still more closely the parallelism between the reversal of phases in emulsions and the precipitation of suspensoids by electrolytes, it was considered desirable to investigate the effect of dilution on the stability of emulsions. The effect of dilution on the precipitation of suspenoids by electrolytes has been studied by Woodstraw, Mukherjee, and theoretically by Smoluchowski. The table of results shown below indicates the change in the rate of coagulation on dilution (Mukherjee and Sen, 115, 464, 1919, *J.C.S.*).

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TABLE 5

Sol A contained 17·58 *millimoles of arsenious sulphide per litre. Sol B was prepared by diluting sol A five times, and sol C by diluting sol A ten times, with pure water.*

Electrolyte : lithium chloride

Dilution (after mixing).	Sol A.	Sol B.	Sol C.
5N/16	—	—	Coagulation after 20 seconds.
5N/32	—	Coagulation after 30 seconds.	Coagulation after 50 seconds.
N/8	Instantaneous coagulation.	Coagulation after half an hour.	Perceptible change after 8 minutes. Coagulation after 2¼ hours.
N/16	Change perceptible on mixing. Coagulation not observed after 1½ hours.	Change just after mixing not perceptible.	Change perceptible after 45 minutes.

The results obtained for emulsions also point to the fact that the greater the dilution or the distance between the oil particles in an emulsion, the larger the amount of the polyvalent electrolyte required to bring about the reversal of phases. These results indicate a parallelism between the reversal of phases and the precipitation of suspensoids by electrolytes. A few observations were also made to see how the rate of coagulation of the typical natural emulsion, milk, is affected by dilution. The following table shows some of the results obtained.

TABLE 6

Vol. Solution always 20 c.cs.	Time for First perceptible Change on the addition of a known amount of H_2SO_4.
Pure milk - -	Immediately after adding.
Twice diluted -	9 minutes 2 seconds.
Thrice diluted -	12 minutes.
Four times diluted	15 minutes 3 seconds.

It is thus evident that even in the case of milk, the greater the dilution the stronger is the acid required to bring about an immediate perceptible coagulation change. The fact that the quantitative results in case of reversal are not of the same order as in precipitation of colloids, indicates that, besides the electrical change in the film surrounding the globules, some chemical change also takes place. The nature of the film can be changed chemically, or electrically, *e.g.*, $Fe(OH)_3$ reverses the type, perhaps by merely changing the charge on the protective sol. A protective sol which is positively charged tends to stabilise, as water in oil emulsion. All negatively charged protective colloids, like sodium oleate, gelatine, casein, etc., form oil in water emulsions. Electrolytes like $Ba(NO_3)_2$ $AlCl_3$, etc., form bivalent and trivalent soaps which are positively charged and, therefore, change the type of the emulsion.

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A complete study of the effects of electrolytes, the degree of dispersion, and the distance between the particles in these emulsions, points to the conclusion that the character of emulsions as model suspension colloids is not destroyed by using soap solutions as stabilising agents, and that the latter may be regarded merely as protective colloids. The theoretical interest arising out of the problem is great. The observed parallelism between the reversal of phases in emulsions, and the precipitation of colloid sols in suspensions, suggests that the cause or causes operating to produce such identical effects may also be identical. A thorough study of emulsions and a comparison of the large amount of data already obtained on simple and well-studied colloidal sols (like gold, As_2S_3, and blood, etc.) in the light of a possible parallelism between them, may lead one day to the clearing up of the mystery of coagulation and prepare a way for a rational theory of colloidal solutions and emulsification.

Apart from the theoretical interest of the problem, a thorough study of the effects of electrolytes on the stability of soap emulsions is likely to be of great practical value. For example, the differences in the amount of electrolytes required to bring about the reversal of phases with different soaps points to the probability of a difference in their protective actions.

The results obtained for B.P. paraffin oil indicate that the soaps can be arranged in order of their protective action as Pot. Stearate> Sod. Stearate>Sod. and Pot. Palmitate>Pot. Oleate>Sod. Oleate. The results have an important bearing on the washing power of soaps. Provided the water is free from electrolytes, the cleansing power of these soaps may also be in the same order. The old hypothesis of Chevruel that the cleansing power of soap is due to the free alkali liberated is now discarded in the light of recent extensive investigations of MacBain (*J. Soc. Chem. Ind.*, **37**, 249 T, 1918). According to the modern conception the washing power of soap is due to its emulsifying efficiency, or, better, to its protective action, which keeps the dirt and grease bound in the form of an emulsion. A complete investigation of the emulsifying efficiency of various soaps for the more common dirts, like dust, soot and grease, will be of very great practical importance for the soap industry. On this view, the cleansing properties of soaps should be considerably affected by the electrolytic impurities in water, and traces of Ca, Barium, and trivalent salts will be injurious for cleansing purposes, as they would tend to form a water-in-oil emulsion which is sticky and difficult to be washed with excess of water. My best thanks are due to Professor Donnan for his kind advice and assistance.

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DISCUSSION

Prof. H. R. Procter : I do not wish to criticise anything that has been said, but merely to add a small fact which has come to my knowledge, and which may be of interest to some people who have been engaged in the subject. We have been making experiments in my laboratory upon the surface tension lowering of solutions of sulphonated oils. That is a practical question in the leather trade, and also has general bearings. We have been making these experiments by the ordinary method of dropping a mineral oil below the surface of a solution of sulphonated oil, and we find that the surface tension is largely dependent upon the exact hydrion concentration. It rises steadily with increasing hydrion concentration up to a certain point, at which it reaches a maximum and then begins to diminish, so that there is a point somewhere between the alkalinity and acidity, a point in the wide region between the colour change of methyl orange and the colour change of phenolpthalein, at which the surface tension in this particular case is at a maximum.

Mr. E. Hatschek : I think that Mr. Bhatnagar's parallel between the reversal of phases in emulsions and the precipitation of suspensoids by electrolytes may be questioned, and there may be an alternative explanation. What the thing really turns on is the relative solubility of the fatty acid salt formed in water and in oil. The fatty acid salts of the tri- and some bi-valent cations are soluble in oil, while those of the univalent ones are soluble in water. If a film of oil-soluble soap is substituted for the film of water-soluble soap, it seems to me that reversal of the phases would naturally follow, provided both are present in sufficient amount. In this point, too, the parallel with suspensoids fails, as none exist in which the phase ratio even remotely approaches 1 : 1.

Prof. J. W. McBain : The results obtained by Mr. Bhatnagar show no parallelism between protective action and solubility of the soaps in aqueous phase. I have no knowledge of the relative solubilities in oil of the soaps examined; perhaps someone else has that information.

Prof. W. C. McLewis : I was particularly interested in one point Prof. Donnan raised, namely, that one could get a stable emulsion with two absolutely pure phases. I would like to ask Prof. Donnan for a little more information on that point, because I have got an idea that ultimately the stability will depend upon the presence of at least one further substance. Of course, in the case which Prof. Donnan cited, oil and water, under conditions in which the oil and water were extremely pure, you cannot avoid having the ions of water there, and I would like to know if his idea is that, even in that case, the ions would be the stabilisers. Another point with regard to emulsions in general : emulsions can be de-emulsified by the ions of electrolytes, and the de-emulsifying action depends upon the valency. Hitherto, of course, comparisons have been drawn in terms of concentration, *i.e.*, we have compared the de-emulsifying powers of various electrolytes of the same concentration, but the

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idea which suggests itself to me is that we should compare electrolytesi not at the same concentration, but at the same thermo-dynamic activity. I will not go into the question of thermo-dynamic activity, but, as you know, it has thrown a great deal of light on many other problems, and it seems to me that it is quite probable that work in other fields dealing with the measurement of thermo-dynamic activity of various ions might, if brought into the field of emulsions and of colloidal solutions, tend towards a revision of our knowledge as regards both coagulative and protective effects. There is one other point, and it is one raised by Mr. Clayton and one he would have dealt with had he been here. Nearly all emulsions and colloidal solutions are electrically charged and, as a rule, the ions with the opposite charge have a coagulating power. Mr. Clayton, however, considers that he has found a case in which a suspension can be coagulated by a colloid of the same electrical sign. If this is really the case, the observation becomes one of the greatest importance as it certainly would diminish greatly the value of the so-called electrical view of stability of dispersed systems. It has always been a moot point as to how far we should consider such phenomena as electrical or as capillary. Probably, ultimately we shall have to bring in both effects though, of course, that helps us very little at the present time, in view of the fact that the theory of electro-capillarity is so very little developed. In connection with Mr. Clayton's observation, I would draw your attention to the behaviour of a benzene emulsion. You can make an emulsion of benzene in water containing a very little gelatine and obtain a highly concentrated emulsion. The benzene is

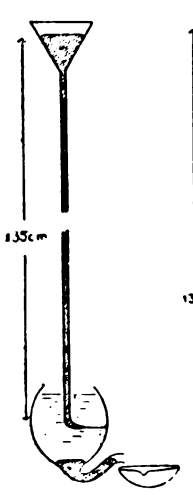

FIG. 1.

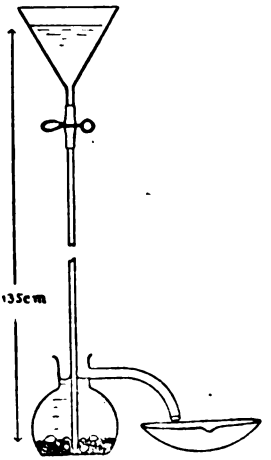

FIG. 2.

the disperse phase. Further, it can be shown that the benzene particles are negatively charged. This emulsion can be de-emulsified by hydrogen ion, and also by hydroxy ion. The effect of the hydrogen ion is to be expected; that of the hydroxyl ion is quite unexpected. In this case, however, the paradox is easily explained. What happens probably is that the caustic soda attacks the protecting gelatine, and the emulsion becomes de-emulsified by removal of the stabiliser and not by a direct action of the hydroxyl ion. How far other anomalies might be brought into line is an open question.

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Dr. T. Svedberg : I should like to call attention to a special case in the emulsifying of mercury. The rather striking experience was made by a friend of mine, Dr. I. Nordlund, at Upsala. This experiment is of interest because it shows that there are two different methods of preparing emulsions of substances that have a very high surface tension. If mercury is pressed through a glass tube into water in form of a fine jet striking against a glass wall (Fig. 1), you get a mercury-water emulsion with rather coarse particles. On the contrary, if you press water through the mercury (Fig. 2), there are formed, as the water bubbles rise to the surface, thin membranes of mercury, and these lamellæ when bursting produce very fine particles. Thus a real, though very diluted, mercury hydrosol, pale yellowish-brown in colour, is obtained. In order to prevent coagulation and maintain the primary structure, a trace of potassium citrate should be added to the water (suitable concentration : 0·0025 normal).[1] I have repeated the experiment with oil and water, but in this case no difference was found between the products obtained by the two procedures.

Prof. Procter : With regard to Mr. Bhatnagar's paper, there is an extraordinary similarity between the structure he describes and the structure of connective tissue. The connective tissue consists of fibres, made up of small fibrils of about 1 μ in diameter, parallel to each other, and apparently these are not living cells. They have no nuclei, but seem to be produced by the cells which exist among them, and which possibly move along the fibres.

[1] *Koll-Zeitschr.*, 26, 121, 1920.

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SECTION II.—THE PHYSICAL PROPERTIES OF ELASTIC GELS

The Introductory Paper to this Section of the Discussion was given by **Mr. Emil Hatschek.**

THE PROPERTIES OF ELASTIC GELS

BY

EMIL HATSCHEK, F.INST.P.

The statement that the familiar table jellies (gelatine gel) are typical representatives of the class to be discussed in the present paper will probably, at the outset, be found more useful than an attempt at strict definition. These systems exhibit immediately two of the most characteristic properties of the elastic gel: stability of shape, notwithstanding a very high content of liquid (about 95 per cent. in the case quoted) and perfect elasticity within certain narrow limits.

The gel may be obtained in two opposite ways: either by transformation—which may be reversible or irreversible—of a sol, *e.g.*, by cooling a gelatin sol below a certain temperature; or by allowing the dry substance to "swell" in an appropriate liquid. Practically all substances from which elastic gels may be produced show this capacity of swelling, though to an extent which differs widely. Only certain liquids will cause a given substance to swell, and the relations between the constitution of the solid and the liquid, on which this property is based, are at present quite obscure. Thus gelatine and agar (the former a protein, the latter a mixture of carbohydrates) swell in water at ordinary temperature, but do not dissolve until the temperature is raised. Vulcanised india-rubber swells in various organic solvents such as benzene, toluene or xylene, without dissolving. Finally, the processes of swelling and dispersion or solution may proceed *pari passu*, as with gum arabic at ordinary temperature. At low temperature, a definite stage of swelling may be observed to precede solution.

The elastic gel which can be most easily reproduced and has, accordingly, been studied most frequently and extensively, is that of gelatine. Bodies of any desired shape can be obtained by pouring the gelatine sol into suitable moulds and allowing it to set for a period of not less than 24 hours (*cf. infra*, E. Fraas). The procedure, once chosen, must be rigidly adhered to throughout, since all the properties of a gel depend, not only on its composition, but also to a marked extent on its history, especially its "thermal history," *i.e.*, the temperatures to which the sol has been exposed and the duration of such exposure. Some of the principal investigations will now be briefly summarised.

ELASTIC PROPERTIES

These have been studied principally by R. Maurer,[1] P. v. Bjerken,[2] E. Fraas,[3] and A. Leick.[4] All these investigations date back some time, and were undertaken with a view to studying a material with very low modulus and sufficiently transparent for examination in polarised light, rather than with the intention of elucidating such

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problems as the structure of gels. Both Maurer and Leick determined Poisson's ratio for gels of various concentrations and find it 0·5 within the limits of error—a result which is not surprising in view of the large percentage of liquid. Maurer studied the elongation of gel cylinders of considerable diameter (2·21 cm.) with small loads, the extensions being measured microscopically. His figures for the modulus are in good agreement with those found by Leick, which range from 2·42 (gm/mm²) for 10 per cent. to 29·4 for 45 per cent. gels. Leick found the modulus E roughly proportional to the *square* of the gelatine concentration; the ratio E/c^2, however, varies somewhat irregularly, and decreases with increasing c. All the investigators find that the modulus increases with increasing load.

Fraas studied the ageing of gels and found that a constant modulus was not reached until about 24 hours after apparently complete setting. These hysteresis effects are universal in colloidal systems, and the increasing modulus of a gel is paralleled by the increasing viscosity of the sol, when kept at a temperature above the setting point. In the following table one series of Fraas's results is given to illustrate the magnitude of the effect.

Cylinder of 20 per cent. Gelatine Gel

Hours after removal from mould	1	2	3	4	5	6	7	24
Extension produced by 50 gm. weight	12·5	7·5	7	7	6·5	6·5	6	5

Maurer, and more particularly Leick, also studied the effect of various substances dissolved in the water on the elastic modulus of gelatine gels; the results are of particular interest from the colloidal point of view, inasmuch as they can be co-ordinated with the well-known effects of such solutes on other properties of the system, *e.g.*, maximum swelling, setting point of sol, &c. Leick finds that the addition of various chlorides lowers the modulus, sodium sulphate is without action, while cane sugar and glycerine raise the modulus considerably. Chlorides also lower the viscosity and setting temperature of the *sol*, while glycerine and cane sugar (generally substances containing hydroxyl groups) raise both constants.

The elasticity of gels is perfect only for small loads applied for a short time, but very little work has been done on relaxation in such systems. A. O. Rankine[5] maintained gelatine gels of low concentrations (3·4 to 4·5 per cent.) at constant strain and plotted the stress necessary to do this against time. The stress, within the limits of concentration and time investigated, never becomes zero. Breaks occur in the time-stress curves, which are taken to indicate that the elastic limit has been reached. The concentrations employed by Rankine are very much lower than those at which determinations of the modulus, &c. have been made.

Reiger[6] determined the relaxation time of gelatine gels by optical means (disappearance of the double refraction produced by strain). The investigation was undertaken with the object of testing Maxwell's relation between modulus, viscosity and relaxation time, and was accordingly carried out at 29° C., *i.e.*, at a temperature very near the " melting point " of the gel. In these conditions Reiger found a relaxation time of 10 minutes for 20 per cent., and about 41 minutes for 40 per cent. gel.

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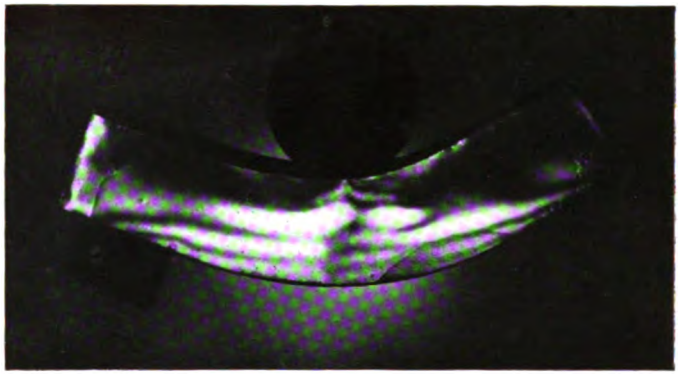

FIG. 1.

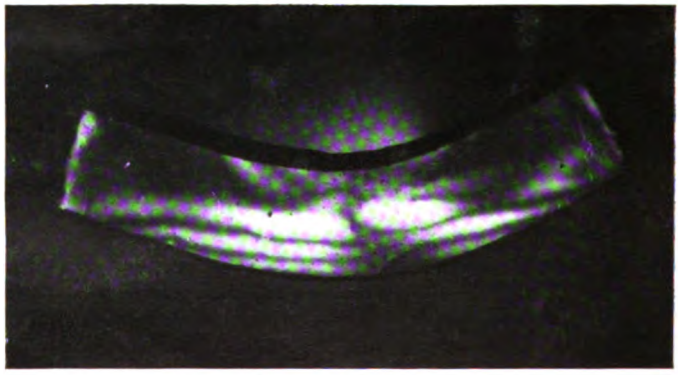

FIG. 2.

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That the conditions are entirely different at lower temperatures is shown by experiments by the writer, published here for the first time. Rectangular prisms of gelatine gel (10 per cent.) with 1 per cent. of sodium fluoride, to prevent putrefaction, were cast and allowed to set for 36 hours before removal from the mould. One of these prisms was then bent between three stops fixed on a glass plate, the latter being covered with paraffin oil to prevent adhesion of the gel and consequent irregular deformation. The specimen was then photographed in polarised light (double plate glass as polariser, Nicol as analyser) within 10 minutes of the application of stress at room temperature, about 15° C. This photograph is shown in Fig. 1. The glass plate with the specimen was then placed in a moist chamber for five days, being examined at intervals (visually) without any noticeable change showing itself. At the end of five days the stress had practically disappeared, so that the specimen could be removed without friction and without straightening itself appreciably. It was then again placed on an oiled glass plate and photographed as before, the result being shown in Fig. 2. Considering the extreme sensitiveness of 10 per cent. gel to deformation, it may be said that the appearance is substantially unaltered, and that at any rate the optical anisotropy caused by strain has not disappeared with the removal of the stress. The absence of relaxation in a system consisting to about 90 per cent. of liquid is certainly remarkable and will be referred to again.

Optical Properties

The double refraction produced by deformation has been referred to incidentally in the preceding paragraph. Quantitative investigation of this property has been carried out chiefly by Leick (*l.c.*). His principal results (obtained with gel plates in tension) are: (1) the double refraction ($D = n_r - n_u$) is, *cæteris paribus*, very approximately proportional to the strain, and (2) for equal relative elongations the double refraction is roughly proportional to the gelatin content.

The refractive index of both gelatine sols and gels has been shown by G. S. Walpole[7] to be a linear function of the gelatine concentration. If the refractive index is plotted against the temperature over a range containing the setting point, no discontinuity occurs at the latter, *i.e.*, when the sol is transformed into gel.

On the whole, our knowledge of the elastic and the related optical properties of gels must be pronounced slight. As in other branches of the subject, non-aqueous systems have received hardly any attention; their study is eminently desirable, as the enormous complications introduced in the case of a protein like gelatine by the formation of salts, and their electrolytic and hydrolytic dissociation, would be absent. There is a very large literature on the stress-elongation curve of india-rubber, which, however, refers only to the dry material and is not of immediate interest. The writer has found only one reference to a rubber gel in a paper by A. E. Lundal,[8] who determined the tensile modulus of rubber which had imbibed 133 per cent. of paraffin oil and found it about one-half that of the dry material.

Diffusion in Gels

This phenomenon has, for various obvious reasons, received a considerable amount of attention. Thos. Graham already used dilute gels instead of pure aqueous solutions in the study of diffusion, and found the rate approximately the same in both. This, however, only holds good of gelatine gels up to, say, 3 or 4 per cent. and agar gels

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under 1 per cent. In more concentrated gels the rate of diffusion decreases markedly with the concentration, but no quantitative relations have, so far, been determined. The rate of diffusion for a given solution and gel concentration can be affected by various solutes in the latter. Among the earliest investigations on the point are those of H. Bechhold and J. Ziegler[9], who found NaCl and NaI without effect; Na_2SO_4 and several non-electrolytes as dextrose, glycerin and alcohol reduced the rate of diffusion of certain solutes. A certain—though not exact—parallelism shows itself between the effect of solutes on the elastic modulus and the rate of diffusion: substances which increase the former reduce the latter. The experimental difficulties are very considerable and are explained in the literature. Among more recent papers on the subject are those by O. v. Fürth and F. Bubanovic,[10] and by W. Stiles.[11]

The fact that both the swelling and the drying of gels are controlled by diffusion involves some consequences which, considering that they may have an important bearing on histology and related subjects, have not yet received adequate attention. If a body of gel is bounded by a surface in which the radius of curvature changes very quickly or (as in polyhedra, cylinders bounded by plane ends, &c.) discontinuously, diffusion to or from regions adjacent to tracts of surface with low or zero-radius takes place more rapidly than from the rest. The result is that a body of gel does not remain similar to itself during swelling or drying, but undergoes successive deformations which may be considerable. The effect is particularly marked in drying; thus, cylinders with plane ends at first dry more rapidly round the circular edges, which contract, the profile becoming that of a barrel with convex ends. As the material forming the edges becomes less permeable, the large surfaces dry more quickly, and the final shape is, approximately, a single-shell hyperboloid with concave ends. On allowing such a body of dry gel to swell again, the original shape is not necessarily restored; the reason for this alteration in the capacity of absorbing water is obscure.[12]

The foregoing summary—though necessarily restricted by considerations of space—may give the reader unfamiliar with the literature some idea of our present knowledge. The two great problems to be solved must now be set forth briefly. They are (1) the elucidation of the structure of elastic gels, and (2) the explanation of the phenomenon of swelling. As regards the former, there is at present a fundamental divergence of opinion, inasmuch as some authors (H. Procter, W. Pauli, and J. R. Katz) maintain that elastic gels are *homogeneous* systems, *i.e.*, solid or (H. Procter) " semi-solid " solutions. The evidence for this view is set forth at length in a very exhaustive monograph by Katz.[13] The other school (W. B. Hardy, Wi. Ostwald, Wo. Ostwald, S. C. Bradford, Dorothy J. Lloyd) consider gels to be heterogeneous systems, but differ regarding the state of aggregation of the phases. Ostwald, in particular, considers gels to be *systems of two liquid phases* having an interfacial tension, while some of the other investigators incline to the view that the properties of gels are best accounted for by assuming some sort of network or cellular arrangement of *solid* phase permeated by liquid. Speaking generally, these rival theories are based on the consideration of a limited number of selected properties, and a great deal of further work is required, probably on quite novel lines, before a definite conclusion commanding universal acceptance can be reached. The author feels, in particular, that the elastic properties have received insufficient attention, and

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has attempted, as a first step, to examine whether they are compatible with the assumption of two liquid phases possessing interfacial tension,[14] the result being negative if the assumptions necessary to allow of mathematical treatment are granted.

As regards the phenomenon of swelling, we have at present no explanation whatever why certain substances swell in a comparatively limited number of liquids. In the case of proteins, which have received the greatest attention, conditions are enormously complicated through salt formation and electrolytic and hydrolytic dissociation, and here, as in other problems of colloid chemistry, substantial progress is to be expected only from the study of non-aqueous systems, of which a large number is certainly available. This is also the view expressed by Katz in the monograph already quoted: "Swelling in organic solvents would, perhaps, be more important for an investigation in the service of pure physical chemistry than swelling in water." It is greatly to be hoped that the present discussion may induce competent workers to examine this—equally neglected and promising—field.

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[1] R. Maurer, *Ann. d. Phys.*, **28**, 628, 1866;
[2] P. v. Bjerken, *ibid.*, **43**, 917, 1891.
[3] E. Fraas, *ibid.*, **53**, 1074, 1894.
[4] A. Leick, *ibid.* (Drude), **14**, 139, 1904.
[5] A. O. Rankine, *Phil. Mag. Ap.*, 1906, 447.
[6] R. Reiger, *Phys. Zeitschr.*, **2**, 213, 1901.
[7] G. S. Walpole, *Koll. Zeitschr.*, **13**, 241, 1913
[8] A. E. Lundal, *Ann. d. Phys.*, **66**, 741, 1898.
[9] H. Bechhold and J. Ziegler, *Zeitschr. phys. Chem.*, **56**, 105, 1906.
[10] O. v. Fürth and F. Bubanovic, *Biochem. Zeitschr.*, **90**, 265; **92**, 139, 1918.
[11] W. Stiles, *Biochem. Jl.*, **14**, 58, 1920.
[12] E. B. Shreve, *Science*, **48**, 324, 1918; *Jl. Frank. Inst.*, 187, 319.
[13] J. R. Katz, *Die Gesetze der Quellung, Koll. Zeit.*, IX., 1917.
[14] E. Hatschek, *Trans. Faraday Soc.*, Vol. XII., Part 1, 1916.

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THE STRUCTURE OF ELASTIC JELLIES

BY

PROFESSOR H. R. PROCTER, D.Sc.

When I was invited to take part in this discussion, I expressed the desire not to be entrusted with the responsibilities of an introducer, but to leave this in younger and more vigorous hands. As, however, I have been put down for the part, I will endeavour to fulfil it as best I may, and appeal for indulgence in any inevitable shortcomings.

I take it that the three possible views of such a structure are—

1. That of a simple emulsion of spherical or more or less distorted globules in a liquid medium.

2. A sponge-like structure, containing in its pores either the suspension liquid, or a liquid solution of the colloid, but two-phased in the sense that the pores are of microscopic and not molecular dimensions, and open ended, and that the two phases are therefore chemically independent and mechanically separable.

3. A more or less solid solution of the exterior solution in the colloid, in which both constituents are within the range of the molecular attractions of the mass, and which are in chemical and electric equilibrium with the external liquid when one exists. Such a solid solution therefore constitutes a single phase in equilibrium with a real or virtual external solution.

I take it that the first of these conceptions so little explains observed facts that it is now no longer maintained, and that I may devote my time to the consideration of the two remaining, which mainly differ on the question of size, since both postulate or admit a network framework. The difference, however, is not unimportant, since microscopic size excludes or complicates the simple chemical causes which are sufficient for the solid-solution view, and involves mechanical structure which itself demands explanation. Of course the molecular view does not preclude the possibility of there being microscopic pores, closed or open to the surface, but it does not assume that they take part in the equilibrium. Such interstices can undoubtedly be produced under certain conditions.

Let me now make clear my conception of the chemical or molecular theory, which demands no assumption but that of the chemical and physical laws which are everywhere accepted.

For the sake of simplicity I will confine myself to gelatine as the elastic colloid, and to solutions of hydrochloric acid on the acid side of the isoelectric point, and so dilute that without sensible error we may assume them as fully ionised, or at least of equal ionisation to the gelatine chloride. Gelatine under these conditions acts as a weak base, and combines with acid to form an ionisable salt, but as the base is a very weak one the salt is freely hydrolysed, and can only exist in presence of excess of free acid. The jelly-mass will therefore consist of gelatine chloride, free acid, and neutral gelatine, in proportions which are determined by Wilhelm Ostwald's well-known hydrolysis equation, and the concentration of the external acid solution. There is every reason to assume that neither the neutral gelatine nor the

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gelatine ion exert any sensible osmotic pressure, though, if they do so, it will only somewhat increase the swelling of the jelly. Now the external acid contains H^+ and Cl' ions in equal numbers, while the jelly contains not only the equal numbers of H^+ and Cl' ions of its free acid, but the Cl' ions of the ionised gelatine chloride, and therefore Cl' ions in considerable excess of the H^+. Now osmotic equilibrium demands that the sum of the diffusible ions in the liquid and the external solution should be equal, while the thermodynamic equilibrium used by Donnan requires that the products of $H^+ \times Cl'$ must also be equal in both, and as the sum of two unequal numbers is always greater than that of two equals giving the same product, it is impossible with finite quantities to fulfil both equations simultaneously, and there must always be a small excess of osmotic pressure in the jelly, which causes it to swell. Of course under these conditions the jelly would tend to swell to infinity and ultimately dissolve; and since it does not do so, we must assume some opposing force, and the only possible one appears to be the elastic cohesion of the jelly, which implies some sort of connected structure. This force obeys Hooke's general law of elasticity, that "the stress is equal to the strain," and in this case increases in proportion to the volume of swelling, and it may therefore also be stated that the energy opposing swelling is equal to the surface-energy created by a real or virtual extension of the surface proportional to the increase of volume. By this is not meant that an actual extension of surface actually occurs, but that the attractive forces of the molecules which constitute the "internal pressure," have been overcome to a similar extent. This generalisation which, if true, applies to all cases of volume-elasticity of a like kind, has an interesting corollary. Surface-tension, as shown by Stefan's law, has a simple relation to the heat of volatilisation, and therefore elasticity must have a similar relation. This should also imply a relation between the elasticity of a jelly and its heat of melting.

I have purposely avoided all mathematics in what I have said, but the fact remains that all the phenomena of gelatine swelling are connected by quite simple equations derived from its chemical equivalent weight and ionisation-constants only, and that curves plotted from these equations agree within experimental error with experimental results. Such concordance cannot be fortuitous, and is not shown by any other theory yet proposed.

As to the nature of the network I postulate nothing, but it must be a very open one, since diffusion takes place through it with almost the same speed as through still water, and considering the chain-character of proteids, it seems not unlikely that the act of "setting" consists in the formation of tenuous and possibly flexible crystals, which interlace and possibly anastomise. Melting them would consist in the breaking up of this complex into smaller and smaller fragments, with increased dispersity and lessened viscosity with rising temperature, and over 70° C., the solution becomes probably nearly molecular. The slow increase of viscosity with time at lower temperatures would depend on the comparative slowness of crystallisation.

It is now in place to point out a few of the difficulties of the sponge-structure theory. Firstly, if the liquid phase is contained in open pores, its ionisation cannot produce an internal osmotic pressure, since there is no semipermeable surface, and nothing to prevent its diffusing into the outer liquid. Also Donnan's membrane-potential theory is inapplicable for the same reason, and because it depends

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on electrical attractions and repulsions which are only operative at molecular distances, and is an equilibrium between two phases only, and not, as in the sponge structure, between three. Though it has hitherto proved impossible to make a direct measurement of the Donnan potential, it is easily calculated when the ionic concentrations are known, and in the case of gelatine and acid only amounts to a few millivolts, and it can be shown experimentally that when it is opposed to an E.M.F. of the same value no current is produced and the combined E.M.F. is zero.

Miss D. J. Lloyd's view that the solid phase of the sponge-structure is composed of isoelectric gelatine also presents difficulties, since the firmness and contraction of the jelly increases with addition of acid beyond the point of maximum swelling, and in N/10 acid is a firm and consistent jelly, while it is shown by the combination curve that at this point the conversion into gelatine-salt is almost complete.

The phase law, if it is applicable to these equilibra, also tells against the two-phased structure, which with a liquid phase forms three phases, with three constituents, gelatine, water and acid (or base), and therefore only two "degrees of freedom," while it is known that temperature and the concentrations of acid and water are all variables. It may be here noted that the phase-law also gives a possible explanation of the Paul von Schroeder effect if it really exists. By bringing the jelly from complete immersion in water into its saturated vapour, a third phase is introduced, and one of the freedoms disappears, so that it is quite possible that equilibrium with the vapour can only exist at one particular degree of swelling.

Perhaps in conclusion I may mention one or two cases in connection with the structure of jellies in which I think experimental results have been misunderstood, or misinterpreted. The first of these is the fact that water, or a weak proteid solution, can be squeezed out of jelly by mechanical pressure, a fact which I observed accidentally some 30 years since in a technical experiment on the filter-pressing of gelatine solutions, and which has been held to prove the two-phased character of the jellies, but which, of course, might have been foreseen as a necessary consequence of ordinary osmotic laws. A jelly behaves exactly like an osmotic liquid confined in a semi-permeable membrane, say like dilute alcohol contained in a bladder. Placed in water this will swell till the osmotic pressure of the alcohol is balanced by the elastic tension of the bladder, but if to this a mechanical pressure be added, a corresponding portion of the water will be expelled, possibly with a little alcohol also, as the semi-permeability of the bladder is not quite perfect. In the same way water is expressed from the jelly, and as commercial gelatine always contains some soluble products of its hydrolysis, some portion of these will be expelled with it.

Another mistaken conclusion is that the progressive combination with acids as the latter are concentrated proves the existence of a large number of combining basicities, which gradually come into action. Such a gradual formation of the gelatine-salt is a necessary consequence of the ordinary hydrolysis law, and if such additional basicites really existed it would be very strange if they did not produce kinks in the regular hydrolysis curve which do not seem to exist. It was to account for such an apparent deviation that I adopted the idea of a second valency, but it was much more probably accounted for by the slight hydrolysis of the gelatine molecule which appears to take place with increasing concentration of acid. There can, I think, be no doubt that the actual combining equivalent is in the

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neighbourhood of 800, though the molecular weight may be much greater, and it is quite possible that this is an average of several proteids containing different amino-acids, but otherwise similar in structure. The number given represents of course only the smallest chemical combining quantity, and it is probable, especially at low temperatures, that the actual molecular weight may be much greater through polymerisation. Paal found a molecular weight of only about 900 by boiling point determinations.

The fact just mentioned of the impurity of commercial gelatine as a single proteid of course renders such attempts as Miss Lloyd's to calculate the molecular weight from the amino-acids found for the present abortive. We are engaged at my laboratory in the attempt to purify gelatine further by separation at its isoelectric point, and perhaps by subsequent fractional precipitation, and if we succeed, shall repeat, van Slyke's determinations.

Leeds, 19 October 1920.

"On the Action of Dilute Acids and Salt-Solutions upon Gelatine," H. R. Procter, *Kolloidchemische Beihefte*, II., Hefte 6–7, 1911; and *Jour. Am. Leather Chemists' Assoc.*, **6**, 270, 1911

"The Equilibrium of Dilute Hydrochloric Acid and Gelatine." H. R. Procter, *J. Chem. Soc.*, **105**, 313, 1914.

"The Acid-Gelatine Equilibrium." H. R. Procter and J. A. Wilson, *J. Chem. Soc.*, **109**, 307, 1916.

"The Swelling of Colloid Jellies." H. R. Procter and J. A. Wilson, *J. Am. Leather Chem. Assoc.*, **11**, 399, 1916.

"Colloidal Phenomena and the Adsorption Formula." J. A. and W. H. Wilson, *J. Am. Chem. Soc.*, **40**, 886, 1918.

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THE REVERSIBLE SOL-GEL TRANSFORMATION

BY

S. C. BRADFORD, B.Sc.

The numerous theories of gel structure fall naturally under three heads. The first class of one-phase, or molecular systems, resembles the "super-cooled liquid" theory of glass, and has difficulty in explaining the loss of mobility which occurs on cooling. The second, or two-phase liquid-liquid, type suffers from the defect that no emulsions are known which have really the properties of gels. Moreover, mathematical analysis shows[1] that this structure does not readily account for the elastic properties of gels. The third, or two-phase solid-liquid, type is the oldest and most natural. It suggests immediately that the almost infinite increase in viscosity which takes place, with slight change of temperature, during gelation is due to the gradual separation of solid from solution and appears to give[2] a simple explanation of all the properties of gels.

In order to understand fully the reversible sol-gel transformation from this point of view, it seems necessary to know the true relation of sols to ordinary solutions. A gradual transition in properties from coarse suspensions through sols to true solutions is generally assumed. This does not readily suggest an explanation of the marked differences in behaviour to electrolytes which occur. It seems probable, however, that sols are related more closely to metastable solutions, the behaviour of supersaturated solutions to electrolytes does not appear to have been studied up to the present. Recent experiments on banded precipitates in gels appear to indicate that supersaturated solutions may be sensitive to electrolytes like sols.

Bechhold[3] had previously mixed solutions of silver nitrate and ammonium chromate in the presence of varying amounts of ammonium nitrate and found that, with increasing ammonium nitrate the precipitate of silver chromate gradually decreased, disappeared, and then gradually increased again. A similar effect was found with potassium sulphate instead of ammonium nitrate. The experiments indicate both a change in the actual solubility of silver chromate and in the metastable limit, since concentrations could be found at which a precipitate was produced only after standing. With citric acid, as a trivalent anion, there was an enormous increase in the value of the ionic product at which precipitation of silver chromate occurred, which varied with the amount of citric acid. When the metastable limit was reached a large excess of chromate was deposited. Experiments in gels indicated a similar effect in the case of potassium citrate and soluble phosphates. The effect may be like that of the hydrogen ion, which tends to prevent the precipitation of positive sols, or of the aluminium ion, which changes the sign and increases the stability of gold sols. The experiments are being continued. So far they afford evidence of considerable sensitiveness to electrolytes on the part of ordinary supersaturated solutions.

If this be so, suspensoid sols would correspond more closely to metastable solutions and emulsoid sols to true solutions. Indeed the characteristic properties of colloid solutions may be due to one

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or both of two separate causes : supersaturation and particle size. From this point of view there should be substances which exhibit colloid properties merely on account of the large size of their molecules, or, of a chemical, or other, tendency to aggregation. Their sols would be comparatively little affected by electrolytes and might be treated as an extreme case of ordinary solutions.

Glutin and δ-galactan appear to fall in this class. The molecular weight of gelatine has recently been estimated[13] at about 10,000, which would give a molecular diameter of $1{\cdot}75\,\mu\mu$. Its rate of diffusion is very low and, consequently, its velocity of crystallisation or separation from solution. From von Weimarn's formula such bodies should form sols on heating and gels on cooling.

For, if such a substance of very low diffusivity be treated with a liquid in which it is only slightly soluble, the Nernst-Noyes formula for the velocity of solution, $V = \frac{D}{\delta} S (L - c)$, shows that, on heating, solution would take place slowly and the sol stage persist. The velocity of crystallisation, on cooling, would also be very small, so that a large excess concentration would be generated, and, if v. Weimarn's formula, $N = K\frac{P}{L}$, applies, P would become great, L small and K a maximum, so that N would be very great and a gel would be formed.

As has been shown,[4] the formula is open to criticism as being merely empirical and the meaning of certain terms somewhat indefinite. And it has been suggested that the equation might preferably be written

$$N = U \cdot \frac{P}{L}$$

where U is a function, to be determined, of the viscosity of the reaction medium and of the size and structure of the particles in solution, whether due to physical aggregation or to chemical complexity. The experimental evidence shows that, as N increases, the precipitate passes through stages in which it appears as (1) large complete crystals only after some years, (2) ordinary crystals in a short time, (3) growth figures or needles, (4) amorphous, frequently showing spherical grains, or spherites, under the microscope, and (5) as a gel which cannot be differentiated by present-day optical instruments. The formula, therefore, offers a reason for the occurrence in the colloid form of such substances as those considered above.

By inoculation of supersaturated solutions, von Weimarn has demonstrated that in every stage, except the two extremes, the solid phase is crystalline ; from which he infers that it is also crystalline in sols and gels. Debye & Scherrer's[5] X-ray analysis confirms this in a number of cases. The special case of gelatine will be discussed below.

Almost all the phenomena of gelation indicate a connection with the process of crystallisation. The properties of supersaturated solutions have frequently been observed in the case of both suspensoids and emulsoids. Gold separates spontaneously from sols of more than a certain concentration, and the precipitation is hastened by the addition of a few drops of a second solution of colloid gold. Gelatine gelates more quickly if solid gelatine be added. Rubber emulsions behave in the same way. The variation of the gelation temperature with concentration[6] strongly suggests crystallisation. And this is supported by the temperature increase in the concentration of solid remaining dissolved in the mother liquor expressed from gels.[7] The crystall-

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isation theory removes the difficulty of explaining the viscosity changes in emulsoid sols in accordance with Einstein's formula, since the changes are due to variation in the number of particles as well as their size. The osmotic pressure changes must be due to the same cause.

Moreover, there are numerous organic substances known which behave exactly as indicated by von Weimarn's formula, and can be obtained as desired in the ordinary crystalline, or in the gel, form. The sodium salt of acrylic acid crystallises from dilute solution as lenticular needles, while the boiling saturated. solution sets to a " structureless " jelly. This seems to be due to a chemical tendency to aggregation. Examples could be multiplied indefinitely.

Except, therefore, that they are not readily obtained in the crystalline form, there seems to be no reason for supposing that gelatine and agar are exceptions to the rule. Gelating 2 per cent. gelatine[8] shows gradual development of submicrons from four or five, showing Brownian movement, in a square division of the field, with a side of 9μ, to 80 to 100 at rest in the same area. If the liquid be expressed from the gel, the submicrons are also visible ultramicroscopically[19]. In the case of reversible gels of 5-dimethylaminoanilo-3 : 4-diphenyl-*cyclo*pentene-1 : 2-dione,[10] the ultimate particles were visible as microscopic spherites of 10μ diameter.

It is therefore to be expected that, by suitable modification of von Weimarn's factors, as, for instance, by reduction in the value of P, it should be possible to obtain the ultimate particles of gelatine of a microscopic size. Although the experiments are still in a preliminary stage the results strongly confirm the theory. In the first experiments, already described,[11] 0·3 and 0·5 per cent. gelatine, sols were allowed to evaporate spontaneously at room temperature. They were only slightly opalescent at first, but developed, within a few days, an extraordinarily dense opalescence with the eventual deposition of a slight buff-coloured precipitate which was seen to consist of spherites up to about $2{\cdot}8\,\mu$ in diameter. Except for the presence of bacteria, the appearance was much the same whether or not 0·1 per cent. mercuric chloride was present as antiseptic. Since the opalescence first appeared within a few hours, decomposition of the gelatine is unlikely. And it was found that warm 4 per cent. gelatine sols do not give a precipitate on standing with saturated mercuric chloride solution. The precipitate must therefore be due to gelatine which has been obtained of microscopic size in accordance with theory.

Experiments under aseptic conditions gave comparable results. Warm 0·4 per cent. gelatine sols were filtered into clean test-tubes, the liquid boiled and the ends of the tubes immediately drawn out and sealed. These similarly, though more slowly, developed an opalescence. In three weeks it had become almost opaque and at the same time the opalescence was observed to be settling down in the tube (Fig. 1). Assuming a density of 1·16 for the falling particles, the rate of fall, 14·9 mm. in 37 days, corresponded to a diameter of about $0{\cdot}1\,\mu$. The microscopical appearance, six weeks later, was that of innumerable grains just too small to be distinguished separately. But a fair number of larger grains were present up to about $0{\cdot}6\,\mu$. In another experiment 0·4 per cent. gelatine, in small test-tubes, was allowed to evaporate at room temperature over concentrated sulphuric acid contained in larger tubes, which were sterilised and sealed. The liquid became turbid and half gelatinous, and had a similar microscopic appearance to that in the previous experiment, though with fewer larger particles

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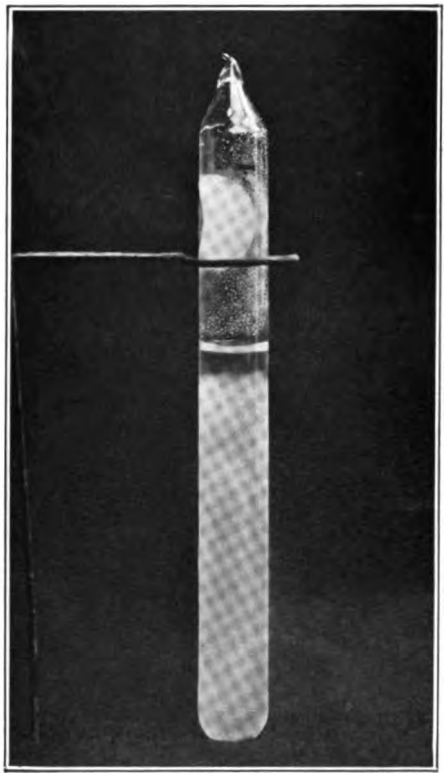

Fig. 1.

x 12606

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N may also be decreased by increasing L by working at higher temperatures. Spontaneous evaporation of 5 per cent. gelatine sols at 31° for 78 hours produced a smoky-looking jelly, which was still viscous in parts, but set on cooling to a stiff mass. The microscope showed this to be full of grains, which were just visible even with a 1-inch objective. Working at 40° gave similar results. With a magnification of 200 the grains appeared perfectly spherical up to about 1 μ in diameter. Many of these were aggregated into clusters somewhat like bunches of grapes. With crossed nicols a glowing point could be made out in the centres of some of the grains. In these experiments camphor was used as antiseptic.

There is, therefore, good reason for regarding the reversible sol-gel transformation as an extreme case of crystallisation, due to the very small diffusivity, and consequent minimum velocity of crystallisation, of the gel substance. With falling solubility on cooling, this necessitates the accumulation of an enormous excess concentration, with great increase of viscosity, and gives a maximum value of N in von Weimarn's formula corresponding to the gel state.

It has already been shown[2] that this view is compatible with all the known properties of gels, as well as indicating new facts. The ultimate crystalline particles of different gels may differ in form according to the nature of the gel substance. The actual structure in a given case is difficult to determine. There are, however, certain phenomena which give some indication of the form of the gelatine particles. It has been shown[2] that complicated organic substances tend to crystallise in the form of spherites. Regarded as an extreme case of twinning, this is obviously the form in which a body can most quickly be deposited. Von Weimarn's experiments show that, as the dispersity of the precipitate increases, the last stage in which the individual grains can be recognised is frequently that of spherical particles. In the experiments described above gelatin always appears in the spherical form. It seems likely that in the gel state the particles of gelatine are also of the same form. This agrees with the gradual increase in the number of discrete particles viewed ultramicroscopically in the gelating sol, and with the ultramicroscopic appearance of the resulting gel. It is further supported by the lenticular shape of gas bubbles in the gel.[12].

Since spherites consist of a great many radiating filaments, if it be assumed that the deposition of solid gelatine occurs when the particles have reached a certain size, it would be expected that, when this limiting size should be reached, the filaments would hardly have attained a cross-section greater than one or two molecules. Such a structure would not give two adjacent planes, in the space lattice of the gelatine molecules, which could give interference of mono-chromatic X-rays, which agrees with Scherrer's results. Or, it is possible that the lack of interference might be due to the great size of the gelatine molecule.

The above considerations suggest a structure for gelatine gels comparable to that of a pile of shot, but, as previously pointed out,[2] they leave open the question as to whether the spherites are themselves united into a framework. The problem is complicated by the fact that the skins of gelatine gels show elastic properties greater than those exhibited by the internal jelly. The formation of the skin is probably due to further precipitation at the surface, due to adsorption and evaporation, so that the gel particles become felted and cemented together. It seems unlikely, therefore, that a gel which had been dried throughout,

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as in the case of ordinary sheet gelatine, would return to its original state by soaking in water. Consequently it is desirable to use freshly prepared gels in experimental work. Almost all the experimental results quoted in favour of a network within the gel could be explained by the presence of the skin, as, for instance, the gradual squeezing out of liquid from a swollen gel.[13] Moreover certain facts appear to indicate that the particles in the interior of the gel are not always united, or are at least easily separated. The lenticular shape of gas bubbles has already been quoted. A gelatine cylinder, hung up by one end in a moist atmosphere, tends to become pear-shaped. Gelatine gels contract in the direction of greatest length when moderately heated, owing to the expansion of the gel within its skin.[2] A gelatine cylinder diminishes in breaking stress on cutting the skin. Three cylinders of 5 per cent. gelatine 24 hours old showed breaking stresses $\frac{(\text{gram})}{(\text{cm}^2)}$ of respectively 16·9, 25 and 25 for the interior gel, and 33, 66 and 133 for the skin, giving a ratio varying from 2·1 to 5·3. On the other hand, aggregation must be assumed in the case of the skin, and insufficient concentration is the only reason why the particles should not grow together within the gel. Crystallisation experiments show a marked tendency of the spherites to aggregation. The remarkable behaviour of the 0·4 per cent. gelatine sols sealed in test-tubes somewhat supports this view. The tubes were not kept in a thermostat and showed a gradual increase in rate of falling of the particles, which may have been due to increase in size. After about 40 days the room temperature was lower and the rate of fall of the particles had diminished considerably. A little later it was observed that the cloudiness below the clear liquid, appeared to have set to a gel, which seemed to be just coherent, but broke up on inverting the tube.

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REFERENCES

[1] Hatschek, *Trans. Farad. Soc.*, 1917, **12**, 17.
[2] Bradford, *Biochem. J.*, 1918, **12**, 351.
[3] Bechhold, *Zeitsch. physikal. Chem.*, 1905, **52**, 185.
[4] Bradford, *Biochem. J.*, 1920, **14**, 474.
[5] Debye & Scherrer, *Physikal. Zeitsch.*, 1916, **17**, 277; Scherrer, *Nachr. Ges. Wiss*, Göttingen, 1918, 96–100, etc.
[6] Pauli and Rona, *Beiträge*, 1902, **2**, 4; Rohloff, *Physikal. Zeitschr.*, 1907, **8**, 442, and Levites, *Kolloid. Zeitschr.*, 1908, **2**, 162, 240.
[7] Hardy, *Proc. Roy. Soc.*, A. 1900, **65**, 95.
[8] Menz, *Zeitsch. physical. Chem.*, 1909, **66**, 137.
[9] Bachmann, *Zeitsch. anorg. Chem.*, 1911, **73**, 150.
[10] Hardy, *Proc. Roy. Soc. A.*, 1912, **87**, 29.
[11] Bradford, *Biochem. J.*, 1920, **14**, 91.
[12] Hatschek, *Koll. Zeitschr.*, 1914, **15**, 226; Bradford, *Biochem. J.*, 1918, **12**, 351; and Osborne, *Proc. Roy. Soc. Victoria*, 1918, **30**, 153.
[13] Lloyd, *Biochem. J.*, 1920, **14**, 147.

NOTE added 29th October, 1920.

The undisturbed gel resulting from the setting of the 0·4 per cent. gelatine solution, described above, was observed to contract beneath the clear liquid. The surface of the gel began to shrink away from the side of the tube, and, in seven days after setting, the whole of one side of the gel had come away from the tube, leaving a clear space of about 1 mm. At the time of writing, the shrinkage was still going on. Since no attempt had been made to adjust the gelatine to the iso-electric point, the shrinkage is of interest in connection with a similar contraction currently described (D. J. Lloyd, *Biochem. J.*, 1920, **14**, 584) of a 1 per cent. gel prepared from iso-electric gelatine.

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THE STRUCTURE OF GELS

BY

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The current view of the constitution of gels is that of fluid droplets of extremely minute dimensions enclosed in a solid framework comparable, in a rough and ready way, to a honeycomb. The idea of this type seems to have had its origin in a suggestion of similarity of gel structure with that of the stems of young plants, which though containing, perhaps, as much as 90 per cent. of water, for the most part enclosed in cells, nevertheless possess considerable rigidity and elasticity.

The earliest attempts to render gel structure visible, which were made with the aid of microscopic methods by Bütschli (1902) and resulted in the display of a foam-like appearance, difficult of interpretation, were unfortunately barren of scientific result. Subsequently the range of microscopic investigation was considerably increased by ultramicroscopic methods, which have now been employed in studying gels by several observers, including Zsigmondy (1912). The result has been to show that gels sometimes are apparently structureless on ultramicroscopic examination, and that when structure is observed this consists, not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection. This fibrillary structure has been studied in gels of soap, barium malonate and fibrin.

The nature of the fibrils and their mode of formation have been the subject of divergent views. Stübel (1914) pointed out their superficial resemblance to linear crystals, and Howell (1916) introduced in this connection the term crystalline gel. Nevertheless, evidence that the fibrils possess the physical characters of crystals is wanting. Barratt (1920), who observed that the fibrils in a fibrin gel are not only remarkably elastic but are also tense, has advanced an hypothesis of their mode of origin from the disperse particles of the sol out of which this gel is formed.

It has been doubted whether gel characters are explicable as the result of fibril formation. This doubt seems to have arisen from the circumstance that, under suitable conditions of experiment, gels in which no fibrillary structure is apparent may be prepared from fibrinogen hydrosol. In my experimental work, however, it has been found that fibrils may be shown to be already formed for a relatively considerable time before becoming visible, being at first amicroscopic and subsequently increasing in size until ultramicroscopic visibility is reached. Moreover, the excessively fine fibrils first seen may, under appropriate experimental conditions, be made to increase in thickness until a diameter exceeding 1 μ has been reached, this increase occurring at the expense of the continuous phase of the fibrinogen sol. It would appear, therefore, that the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic. This type of structure affords

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an explanation of the physical characters presented by gels. If the fibrils are excessively fine and extremely numerous, a gel will be formed which, owing to the enormous resistance offered to the passage of water through the interstices of its fibrils, will appear "dry" and rigid, rather than elastic: if the fibrils are coarse and relatively few in number the gel will be moist, fluid will exude on pressure or on spontaneous "retraction of the clot," and a certain amount of elasticity will be observable. The network character of gel structure renders the behaviour of gels in respect of diffusion readily comprehensible. The fibrillary hypothesis of gel structure also affords a very simple explanation of gel filtration: ultramicroscopic and amicroscopic particles and also, under suitable conditions of experiment, large molecules or radicals may be arrested by gel fibrils in just the same way that microscopic particles are stopped by cotton fibres in filtration through filter paper.

References

Barratt, *Bio-Chem. Journ.*, 1920, **14**, 189; Bütschli, *Untersuchungen über mikroskopische Schäume und das Protoplasma*, Leipzig, 1902: Howell, *Amer. Journ. of Physiol.*, 1916, **40**, 526; Stübel, *Pfluger's Archiv*, 1914, **156**, 361; Zsigmondy u. Bachmann, *Kolloid-Zeitschr.*, 1912, **11**, 145.

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The following contribution to this Section of the Discussion was received from **Professor Dr. Zsigmondy** (Göttingen) in response to an invitation :—

The communications by Messrs. Barratt, Hatschek and Bradford* concern problems which have long been occupying me, and which hence particularly interest me. I have been endeavouring to find methods of helping colloid chemistry out of the undesirable condition in which it has been for a long time, a condition of uncertainty which has rendered it possible that two entirely contradictory views could co-exist and be exposed with equal degrees of probability.

The papers quoted repeatedly refer to ultramicroscopic methods. Mention has also been made of another method[1] of studying gel structures of amicroscopic character. This last method is based upon an examination, after van Bemmelen, of the lowering of the vapour tension which liquids undergo in dry gels. John Anderson,[2] of Glasgow, investigated in this way a gel of silicic acid, and found by careful experiments with several liquids that the gel in question contains hollow spaces of less than 10 $\mu\mu$ diameter. Working by the same method Bachman[3] found later that the gelatin jellies, hardened after Bütschli, likewise enclosed much finer hollows than one would expect after Bütschli's microscopic observations. Similar cavities of two different orders of magnitude also occur in cocoa-nut charcoal. This method of investigation deserves further application.

Already before 1914 the various methods of examination of different experimenters had established that the gel structures may vary much more than had been assumed[4], and that in addition to the apparently grainy structure we meet in the diluted gels of gelatine, agar and silica[5] very frequently also with the fibril structure to which Barratt draws attention, especially in aqueous soap jellies. It should be pointed out that Barratt's observations of amicroscopic fibrils—which only gradually become visible—can also be made in soap gels.[6] This observation, and others of similar nature, support the suggestion thrown out by Flade,[7] that the jellies consist, *in general*, of a texture of (probably) crystalline threads.

This view, however, seems to be contradicted by the ultra-microscopic structure of the diluted gels of gelatine, agar and silica as investigated by Bachmann. In these cases we can observe the formation and agglomeration in flaky groups of freely movable ultramicrons (of so far unknown structure). This phase of gel formation must hence not be regarded as a crystalline process, but as an aggregation of already formed ultramicrons.

If we were to regard the gel formation quite generally as a crystallisation process, then the assumption of Bradford (development of ultramicroscopic spherites composed of crystalline fibrils) would quite well explain the primary process. Certain facts seem still to be incompatible with this view, however, in the case of gelatine.[8] Yet it is to be welcomed that this problem is approaching a gradual elucidation; Hatschek, too, comes to a negative result with his argument that the gels consist of two liquids, and this hypothesis hence appears less and less justifiable.

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On the other hand I do not quite wish to fall in with the generalisation that the gel formation should always, even in its primary stages, be regarded as a crystallisation process. The colloids display far too much variety to admit of their being brought under one general scheme. We may, for instance, accept the standpoint of Nägeli and assume that the gels (jellies as well as fibrous textures) consist of micellæ (anisotropic ultramicrons) and that they break up, when being dissolved, into these constituents, and not into simple molecules.†

I beg here to draw attention to the results of researches which appear not only to support Nägeli's theory, but also, I think, to supply a good basis for the explanation of some other phenomena. The crystalline character of the elements of vegetable fibres had long been doubted in spite of their double refractivity. The crystalline nature of ramie fibre has now been demonstrated by Scherrer with the aid of Röntgen rays. Optically the proof had already been given by H. Ambronn,[10] who has shown, moreover, that the positive double refraction of cellulose turns into a negative refraction on nitration, though the structure of the fibre does not undergo any appreciable change. According to Ambronn this is a case of a pseudomorphosis of nitrocellulose back to the cellulose type. He observed further that the celloidin, obtained by dissolving the nitrocellulose and turning it into a jelly, also shows negative double refraction—when in the stretched condition. With Nägeli and Ambronn I am inclined to assume that nitrocellulose, in being dissolved, does not break up into molecules, or does so at least only to a small degree, the main decomposition being into polymolecular crystalline rods. That view would account not only for the "high molecular weight" of these solutions, but also for the very interesting relation between the viscosity of the solution and the viscosity of its dry residue, which has been pointed out by Sir R. Robertson. We need only assume that nitrocellulose has, in the less viscous solutions, broken up mainly into rod-shaped primary particles, whilst these particles are, in the more viscous solutions, partly united to flaky secondary particles in wide ramifications, to arrive at an explanation of the greater viscosity of the latter solutions and of some other facts. The aggregation of the primary particles to secondary particles would diminish the number of osmotically-effective particles, which would lead to a decrease in the osmotic pressure corresponding to an increase in the apparent molecular weight. The secondary particles enclose ample amounts of the solvent; the volume of the freely-moving particles is hence enlarged, and the viscosity is distinctly raised.[11] When the solution is dried, the irregularly grouped particles will not all come to lie parallel to one another. As a consequence the dry film will enclose ultramicroscopic cavities, and its strength will be diminished.

By offering this presumably useful suggestion I should not like to give rise to the impression that I consider all the riddles of the colloid chemistry of nitrocellulose to be solved in this way. I think, however, that Nägeli's hypothesis, though not always relevant, yet enables us to arrive at a clearer understanding of some colloidal phenomena.

* Dr. Zsigmondy had not seen the papers by McBain and Willows and others when sending in his contribution.—Ed.

† The jelly formation would then be based upon an aggregation, devoid of order, of the structural elements considered to have previously been freely movable and of rod shape.

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[1] Zsigmondy, *Kolloidchemie*, 1st edition, chapter 60 (1912); 3rd edition, chapters 62 to 62 (c), 1920; also Zsigmondy, Bachmann and Stevenson, *Zschr. anorgan. Chem.*, **75**, pp. 189–197 (1912).

[2] J. Anderson, *Inaugural Dissertation*, Göttingen, 1914, and *Zschr. phys. Chem.*, **88**, pp. 191–228 (1914).

[3] W. Bachmann, *Zschr. Anorgan. Chem.*, **100**, pp. 1–76 (1917).

[4] Compare the summary, *Physikal. Zschr.*, **14**, pp. 1098–1105 (1913).

[5] Alcoholic sodium palmitate jelly also solidifies to a gel showing similar ultramicroscopic discontinuities, *Koll. Zschr.*, **11**, p. 154 (1912).

[6] Zsigmondy and Bachmann, *ibid.*, **11**, p. 150 (1912).

[7] Flade, *Zschr. anorgan. Chem.*, **82**, pp. 173–191 (1913).

[8] Scherrer concludes from his Röntgen ray examination that gelatin consists of two amorphous substances; *cp.* Scherrer's contribution to Zsigmondy's *Kolloidchemie* (3rd edition, 1920).

[9] *Ibid.*, p. 408; *cp.* also the photogram, Table VII., bringing the crystalline structure out very well; the individual parts seen are probably very thin amicroscopical parallel fibrils or rod-shaped crystals.

[10] H. Ambronn, *Zschr. f. Wissensch. Mikroskopie*, **32**, p. 43 (1918); *Kolloid. Zschr.*, **18**, pp. 80 and 273 (1916), and **20**, p. 173 (1917); Summary in *Göttinger Nachrichten*, 1919, No. 2, pp. 299–320; Brief Summary, Zsigmondy, *Kolloidchemie*, 3rd edition, p. 112 (1920).

[11] *Cp.* Zsigmondy, *Kolloidchemie*, chapter 27, and v. Smoluchowski, *Kolloid. Zschr.*, **18**, p. 190 (1916). By "freely-movable" particles are here understood both the primary particles and the secondary particles, together with their enclosed liquid.

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DISCUSSION

Prof. J. W. McBain and Miss E. Laing : Soap solutions are probably the simplest examples of gelatinising colloids. They present unique opportunities for precise investigation, because all of their properties are reproducible at will and there is no uncertainty with regard to the constitution or molecular weight of the molecules concerned. It is for this reason that perhaps I may be permitted to refer to some experiments carried out by Miss Laing in the Bristol laboratory which appear to be of general significance for the theory of gels. The following remarks are taken from the summary of a paper which we have recently submitted for publication to the London Chemical Society.

1. We have discovered that a soap solution of one and the same concentration and at any definite temperature may be prepared in three characteristic states; namely, clear fluid sol, transparent elastic gel, and white opaque curd. The latter have often, but erroneously, been called gels.

2. The sol and gel forms of a solution of sodium oleate are identical in osmotic activity, concentration of sodium ions, conductivity and refractive index; this proves that identical chemical equilibria and constituents are present in the two cases. The sol and gel differ only through the mechanical rigidity and elasticity of the gel form.

3. The quantitative identity of conductivity in sol and gel is irreconcilable with all theories of gel structure hitherto advanced, with the exception of the micellar theory of Nageli of 1858, which was resuscitated by Zsigmondy and Bachmann in 1912, and which is strongly supported by many lines of evidence referred to in the present paper. The colloidal particles in sol and gel are the same; but whereas in the former they are independent, in a fully-formed gel they become linked up, probably to form a filamentous structure. It is probably the particles of neutral soap, and not the ionic micelle, that exhibit this behaviour.

4. The formation of soap curd, in clear contradistinction to gelatinisation, is analogous to a process of crystallisation, neutral soap separating from the solution in the form of curd fibres of microscopic or ultramicroscopic diameter. This is shown by the drop in conductivity and osmotic activity and confirmed by direct and indirect analysis in addition to observations with the ultramicroscope. Coagulation is thus sharply distinguished from gelatinisation.

These results are of general applicability on account of the detailed similarity of the properties and behaviour of soaps with that of the gelatine salts and of the silicates.

The paper referred to contains a detailed discussion of the very numerous lines of evidence which support this filamentous, fibrillary or streptococcic structure of gels which is indicated by the study of soap solutions.

Prof. A. O. Rankine : There is one piece of work which has not been referred to. It did not receive publication probably because it took the form of a demonstration before the Physical Society about 12 years ago, but it may have some bearing on the subject.

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The particular experiments consisted of trying to measure the rate at which the viscosity of a gelatine solution in water increased with time. We made a solution of gelatine and water and cooled it quickly to atmospheric temperature. In these circumstances, it showed at first no solid properties at all, but just behaved like a liquid. The solution was then put into the annular space between two concentric cylinders, the outer one of which was rotated at constant speed. The couple arising from viscosity and acting on the inner cylinder was measured from time to time. The rate of increase of this couple was found to follow an exponential law for some time, but the interesting thing is this: that at a certain point, suddenly—a point which could not be very definitely fixed or predicted—there was a very large increase of the couple. I remember that it was suggested in the discussion by Prof. Lees that this was evidence in favour of setting being due to the formation of linkages between particles which had been previously prevented by the fluid motion from joining up until, at the critical point mentioned, they ultimately succeeded in establishing solidity. That is a piece of experimental evidence, possibly of value, but I have to confess that I abandoned the subject of gelatine because the theoretical side of it seemed to present such insurmountable difficulties.

Dr. E. R. Rideal: There is an interesting piece of work being done in the United States at the present time on silica gel, a gel used in industrial work for the adsorption of gases. Patrick, who has worked out different processes for the preparation of the gel, is of the opinion himself that although a gel can be prepared with only 5 per cent. of water, yet on the adsorption of water, the curves which he has been able to obtain, not only with the adsorption of water, but with the adsorption of gases such as sulphur dioxide, and the vapour pressure measurements obtained therefrom, seem to indicate that the swelling of that gel, at any rate, is due to the process of filling by capillaries with different size pores, and he has made quite a good case for that view-point. On the other hand, according to the work which has been done on thin films, which, of course, was originally started by Hardy and has been continued with great success by Langmuir in America, the first action that takes place is the superficial coating of the silica gel or any other gel with the molecules in an orientated form. One can show that in the case of benzene, for example, that the benzene molecule lies flat down under the surface and consists of six carbon atoms, with three double bonds, so that there is a good deal to be said for the orientation hypothesis within molecular ranges, followed by a general adsorption in capillaries on the subsequent addition of more of the dispersing medium.

Dr. T. Svedberg: As I have already pointed out in my introductory remarks, I think the point of the building up of the network is a very essential one in the theory of gelatinisation, and regarding this I should like to tell you of a very interesting experiment which has been carried out in my laboratory by Dr. G. Börjeson. That refers to a non-aqueous gel of an inorganic substance. It is possible to obtain by electric pulverisation—oscillatory current arc—a sol of metallic cadmium in alcohol with particles only 5 $\mu\mu$ in radius. If such a solution is allowed to stand in a glass bottle for some time, the particles are oxidized to a certain degree—but only the surface of the particles—and during that time the solution sets to a jelly.

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You can turn the bottle over and it is quite solid; but if you introduce a glass rod into the solution and make a few movements in it, the system at once becomes liquid again, and the viscosity is scarcely greater than that of pure alcohol.

Mr. E. Hatschek: What is the concentration of the cadmium gel?

Dr. Svedberg: The minimum concentration seems to be about 0·2 per cent., but the phenomenon is more marked at somewhat higher concentrations, *e.g.*, 0·5 per cent.

Mr. S. C. Bradford (*communicated*):

The persistence of the optical strain in a gelatin gel after the removal of the mechanical stress, recorded by Mr. Hatschek, is most curious. This is the more difficult to account for in the absence of a satisfactory explanation of the ultimate cause of the optical appearance. It may safely be assumed, however, that the optical effect is due to the mechanical strain. In this case the crystallisation theory of gelation appears to offer a possible explanation of the phenomenon.

Gelatine and a few other well-known gels are remarkable for their stability. Most substances, which can be obtained in the gel form under suitable conditions, rapidly develop macroscopic crystals. On the crystallisation theory, the permanence of the natural gels is explained by the insolubility, and particularly the very low rate of diffusion, of the gel substances. With lapse of time, however, visible crystals should develop. Evidences of slow crystallisation in silicic acid gels have been observed previously. They have now been obtained in the case of gelatin. Some 5 per cent. gelatin gels were sealed in tubes on 3 August. After about 14 weeks the gels have begun to show a distinct opalescence, as in the case of the dilute solutions of gelatin already recorded. The change has not yet proceeded far enough for the separation of water to be noticeable, though there are numerous drops condensed on the higher parts of the tubes.

It seems, therefore, that there is an extremely slow process of crystallisation taking place in gelatine gels by which the larger particles are continually growing at the expense of the smaller ones. The marked increase in the modulus of elasticity during the first 24 hours is probably due to the very slow rate of separation of gelatin from super-saturated solution which requires this time for completion. It may then not be complete. The crystallisation process which goes on subsequently must be much slower than this.

Since gel substance is being deposited on the larger particles in a gel, whether strained or not, in the former case the larger particles will gradually become cemented in their constrained positions, so that, on removal of the stress, the particles will be unable to move, the gel will remain bent, and the internal mechanical strain will continue to account for the persistence of the optical appearance in polarised light. This experiment appears to establish the presence of a framework within the gel.

Dr. J. S. Anderson (*communicated*):

It may be of some interest to state that Zsigmondy's[1] conception of the structure of the silicic acid gel is supported by the results of an investigation[2] which I carried out in Prof. Zsigmondy's laboratory

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before the war. According to his theory, the silicic acid gel has an extremely fine porous structure, the dimensions of the pores being amicroscopic. By applying the laws of capillarity to van Bemmelen's results([3]) on the hydration and dehydration of the gel, Zsigmondy estimated the diameter of the pores to be about 5 $\mu\mu$, that is, about 200 to 300 times smaller than Bütschli's([4]) estimate of 1 to 1·5 μ. In order to test the accuracy of Zsigmondy's deductions, I made measurements of the hydration and dehydration isotherms and of the similar isotherms for alcohol and benzene in the case of a specially-prepared gel. The results obtained seem to indicate the presence in the gel of pores of various dimensions. In applying the laws of capillarity to the calculation of the sizes of the pores the assumption was made, for the purpose of simplifying the mathematical treatment, that these pores are arranged in the form of fine capillaries. The diameters of the largest and smallest capillaries were found to be as follows :—

	Diameter of largest capillaries.	Diameter of smallest capillaries.
Water experiment -	5·49 $\mu\mu$	2·75 $\mu\mu$
Alcohol ,, -	5·17 ,,	2·42 ,,
Benzene ,, -	5·98 ,,	2·70 ,,
Mean values -	5·55 $\mu\mu$	2·62 $\mu\mu$

The agreement between the values obtained in the three experiments is rather remarkable when one considers that the factors, such as density, vapour, pressure and surface tension, which enter into the calculation, differ considerably in the three cases. The results seem to indicate that at least the order of magnitude is correct; this agrees with other properties of the gel, as Zsigmondy([5]) has pointed out. It is difficult at present to state any definite opinion as to the actual form and arrangement of the pores, but it is probable, as the late Prof. Riecke suggested to me, that the orientation of the molecules of the gel substance is such that the total internal surface of the structure forms a minimum area.

A number of interesting data with regard to the probable mean thickness of the walls of the gel structure, the specific gravities of the dry and wet gel, and the velocities of hydration, dehydration,([6]) &c., are also to be found in my paper.

Mr. W. Harrison (*communicated*) :

There is no doubt that many gels possess fibrilar structure, but this does not apply to all gels. Gelatine and cellulose appear to consist of minute portions joined together in a somewhat irregular manner. Photographs of these have been obtained with the cardioid condenser of Zeiss, using sunlight in the middle of June. The objective used was a $\frac{1}{8}$ in., the camera extension being very long. Better results were obtained in this way than with a more powerful objective.

It is probable that the fibrils present in soap gels are crystalline. Liquid crystals are well known, and gelatinous crystals have been observed on many occasions. For example, benzopurpurine and chrysophenine, two dyestuffs used for cotton dyeing, can be obtained in rigid needle crystals. Concentrated aqueous solutions set to jellies which contain long gelatinous needle crystals, some of these so fine

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that they can pass almost unbroken through a filter paper with the aid of a vacuum pump.

Cholic acid gives a blue precipitate with iodine, which sometimes forms in clusters of needle crystals which are rigid. Under other conditions, one obtains the same needle-shaped crystals quite gelatinous; they may be bent all shapes by moving the cover glass on the microscope slide. The smallest of these crystals show remarkable vibrations due to impact of water molecules. Among these, one often finds spiral-shaped crystals which twist first one way and then the other, as the water molecules bombard them. The movements of these crystals reminds one of the movement of the spiral bacteria present in the teeth.

It is the opinion of the writer that there are many kinds of structures in gels, just as there are many types of structures in crystals.

The observation of Mr. Hatschek that a gelatine jelly, after deformation by stress, retains its optical anistropy after the external stress is removed, is apparently a common property of colloids. The writer made similar observations with indiarubber, cotton, wool, silk and other fibres, but found that the anisotropy was due to internal stresses produced by the deformation and disappeared when the substances were treated so as to allow those internal stresses to balance. (Harrison, *Proc. Roy. Soc.*, A. **94**, 460 (1918).)

Referring to the paper by Mr. Bradford, a photograph was taken by the writer (*J. Soc. Dyers and Cols.*, **32**, 32 (1916)), which shows spherical coagulation-forms of starch which might easily be taken as spherites and which may be analogous to the gelatine spherites mentioned by Bradford. It was found that soluble points in a contact surface had a considerable effect in promoting these growths.

In relation to Bradford's recent experiments on periodic precipitation in gels, the writer made a few experiments some years ago, but has had no time to complete them. One interesting result may be mentioned which does not appear to be explained by the various theories put forward up to the present. Using barium ferrocyanide in a gelatine jelly and diffusing into this a copper sulphate solution, periodic rings of brown copper ferrocyanide and of white barium sulphate were obtained, these rings being alternate. With silver sulphate and barium chloride, alternate rings of silver chloride and barium sulphate were formed.

It does not appear that these experiments can be explained by the super-saturation theory, since both these salts are removed from solution by the precipitation. It appears to the writer that, by the use of salt-pairs which are both removed from the reaction medium, one may learn much more about periodic precipitation.

Mr. E. Hatschek (*communicated reply*): Prof. McBain says in regard to soap gels: "The sol and gel differ only through the mechanical rigidity and elasticity of the gel form." This applies to other gels, and it is therefore all the more desirable to explain the origin of this rigidity and elasticity in terms of some internal rearrangement. The micellar theory does not appear to be helpful in that respect. The first difficulty is that McBain's "ionic micelle" is certainly not the same thing as Naegeli's micelle. It accounts for part of the conductivity of the soap solutions, and if the conductivity of the gel is identical with that of the solution, the ionic micelles must move as freely in the former as they do in the latter. Accordingly, Prof. McBain suggests that "it is probably the particles of neutral

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soap, and not the ionic micelle, that exhibit this behaviour," *i.e.*, that " become linked up." Whether a micellar structure is postulated for the neutral particles as well does not appear.

As regards the identity of several properties in the sol and gel state. this is not confined to soap. Walpole[7] has shown that the refractive index of gelatin sols and gels is the same for a given concentration and temperature : indeed, there is no *a priori* reason why there should be any difference. Arrhenius demonstrated, a long time ago[8], that the conductivity of salt-gelatin water systems was the same in the sol and in the gel condition. As far as osmotic activity —more particularly vapour pressure—goes, there is considerable evidence pointing to their being the same in both states, if they are measurably different from that of the solvent.

As regards " curds," Prof. McBain is, no doubt, right in differentiating them sharply from gels, but the phenomenon is without exact parallel in other typical elastic gels, *e.g.*, gelatine.

The experiment described by Prof. Rankine has often been made with various sols, generally in the capillary viscometer. An exhaustive investigation, *e.g.*, is that by Pauli and Fernau[9] on ceric hydroxide sol, which forms an irreversible gel on the addition of electrolytes. The results correspond with those obtained by Prof. Rankine : they have given rise to the statement to be found in the literature, that the sol-gel transformation (whether reversible or not) is " continuous." This statement simply means that, as far as the rise in viscosity can be measured, a continuous time-viscosity curve is obtained. A point is, however, reached where measurements are no longer possible, and this is the really interesting region, in which a discontinuity is quite possible and indeed probable.

Patrick's results, quoted by Dr. E. R. Rideal, agree with those obtained by Zsigmondy and his school, referred to by Dr. Anderson. It is, however, only the rigid gel—like that of silicic acid or of tanned gelatin—which, on drying, develops pores that are filled with air and can be filled by imbibition with a liquid other than the original solvent (the latter observation was made already by Brewster on tabashir, a silicic acid gel occurring in the internodial spaces of the bamboo). Drying *elastic* gels do not develop such pores : a dry gel of natural gelatin will not imbibe, say, benzene. The dimensions of the pores given by Dr. Anderson are those of the pores in the *dry* gel, and give no clue to the structure of the fresh gel, nor to that of either a fresh or dry elastic gel.

Prof. Svedberg's example is of great interest as showing the very low concentrations of suitable disperse phase, at which gel formation is possible. In this respect they are not unique : Doehle and Rassow[10] have described the mercury salt of an organic sulpho-acid, which forms gels in concentrations of 0·72 per cent., while camphorylphenylthiosemicarbazide, prepared by Prof. M. O. Forster and investigated by the writer, forms stiff gels in concentration of 0.33 per cent. and " trembling " jellies in concentrations as low as 0·25 per cent.[11] Assuming the whole of these concentrations to represent supersaturation, the question arises why similar supersaturations, quite easy to obtain with innumerable other substances, do not lead to gel formation, and what peculiarity of the substance it is on which the phenomenon depends.

Both Mr. Bradford and Mr. Harrison refer to the writer's observations on the survival of optical anisotropy in gelatin gels after the disappearance of the stress. Mr. Bradford's suggestions are quite

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consistent with his views, but there is no evidence of the slow change he postulates continuing beyond the first 24 hours or so. It is, of course, quite possible that such changes occur and that no one, so far, has taken the trouble to look for them. Mr. Harrison has found that a similar behaviour is characteristic of other gels, but this would make it all the more desirable to find the explanation of a phenomenon which is certainly, to say the least, unexpected in a system consisting of over 90 per cent. of liquid. The difficulties of the subject are well illustrated by the investigations of Ambronn on permanently-stretched colloidin strips[12], which were allowed to imbibe liquids of varying refractive index. The accidental birefringence is a function of the deformation and of the refractive indices of both substance and liquid, and may become zero and eventually change its sign when the latter is varied.

Mr. Harrison's suggestions regarding periodic precipitation, viz., the use of salt-pairs which are both removed from the reaction medium, are of great interest and should certainly be followed up.

The writer is also in complete agreement with Mr. Harrison's view that " there are many kinds of structures in gels." There are obvious, and generally acknowledged, differences between the rigid and the elastic gels, to use the current descriptions. There is no evidence that identity of behaviour in either class necessarily implies, still less proves, identity of structure; very eminent authorities like Pauli even consider that many gels are homogeneous systems. Only further research, directed principally to the physical properties, can lead to a solution of this problem.

(1) R. Zsigmondy, *Z. f. anorg. Chem.*, **71** (1911) 356.
(2) J. S. Anderson, Inaugural-Dissertation, Göttingen, 1914; *Z. f. phys. Chem.*, **88** (1914), 191.
(3) J. M. van Bemmelen, *Z. f. anorg. Chem.*, **13** (1897), 233; **18** (1898), 98.
(4) O. Bütschli, " Untersuchungen über die Mikrostruktur künstlicher und natürlicher Kieselsäuregallerten," Heidelberg (1900), 294.
(5) R. Zsigmondy, *loc. cit.*
(6) For an accurate method of measuring such velocities *see* J. S. Anderson, *Trans. Faraday Soc.*, **11**. (1915), 69.
7 G. S. Walpole, *Koll.-Zeitschr.*, **13**, 241, 1913.
8 S. Arrhenius, *Ofvers. d. Stockh. Akad.*, 1885, No. 6, p. 121.
9 Pauli and Fernau, *Koll.-Zeitschr.*, **20**, 20, 1917.
10 Doehle and Rassow, *Koll.-Zeitschr.*, **12**, 71, 1913.
11 E. Hatschek, *Koll.-Zeitschr.*, **11**, 158, 1912.
12 H. Ambronn, *Koll.-Zeitschr.*, **18**, 90, 273, 1916.

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SECTION III.—GLASS AND PYROSOLS

Discussion on "Glass and Pyrosols" was opened with an Address by **Sir Herbert Jackson, K.B.E., F.R.S.**

The following is a brief abstract of the Address, which the author was unable to prepare for publication :—

The lecturer doubted the relevancy of the subject to a discussion on colloids, although he knew of more than one suspension of colouring matter in glass which was colloidal. It was questionable whether glass was crystalline, but there was evidence of some orientation that approximates to crystalline form in a glass when it is phosphorescent. Almost every glass can be made crystalline or made to separate out crystalline material if kept long enough at a particular temperature. The hydration of the borax or other materials used had much to do with the crystallisation of glass on annealing. The study of the physical and chemical properties of glass from the point of view of composition would no doubt yield valuable evidence as to structure.

The remainder of the address dealt with the constitution and properties of opal and coloured glasses.

Dr. M. W. Travers contributed the following Paper on "The Nature of Glass."

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ON THE NATURE OF GLASS

BY

DR. MORRIS W. TRAVERS, F.R.S.

It is commonly stated that glass, in its rigid form, is still a supercooled liquid, the statement being based upon the assumption that its properties change continuously with change of temperature. As a matter of fact, however, this assumption has been based practically entirely upon qualitative observations. Until quite recently no investigations of the physical properties of glasses had extended over any part of the range of temperature within which glass changes from an elastic solid, through a stage in which it may be described as plastic, to that in which its viscosity has fallen with rise of temperature till the glass is a mobile liquid. In 1917 Twyman (*J. Soc. Glass Tech.*, I., 61) published the results of some experiments carried out with a view to testing the application of Maxwell's equation for the disappearance of stress in a viscous body (*Phil. Mag.*, 1868, **35**, 133) to the problem of annealing glass. He investigated the change in the mobility (rate of change of strain with time under constant stress) with temperature, and found that in the case of all glasses investigated the formula

$$dS/dt = Kz^{\theta \cdot 8}$$

held good, the mobility doubling for every 8° rise of temperature. This must probably be regarded as an approximation holding good over the range of temperature within which the glass may be described as plastic.

A few months ago Tool and Valaseck first called attention to a marked discontinuity in the behaviour of glass in the neighbourhood of the softening point (U.S. Bureau of Standards, *Scientific Papers*, No. 358). They found that above a "critical temperature," T_a, which for all glasses examined, including fused boric acid glass, was about 70° below the softening temperature, the rate of absorption of heat with a rise of temperature underwent a sudden increase, which was maintained up to a temperature T_b, slightly below the softening temperature. The range of temperature T_aT_b coincides with what is called the annealing range of temperature, as determined by the optical method, within which the glass may be regarded as plastic.

Following up this work, Cragoe and Peters (*American Optical Soc. J.*, 1920, **8**, 105) determined the thermal expansion of a number of glasses from 20° to the softening temperature. They again found that all glasses, including boric oxide glass, behaved similarly. The coefficient of expansion remained constant from 20° to very close to T_a. At T_a, which was identical with the critical temperature for the glasses examined by Tool and Valaseck, the coefficient of expansion underwent a sudden change in value, again becoming constant, and remaining so over the greater part of the range T_aT_b, but having a value from four to seven times as great as over the lower range. Above T_b the glass appeared to contract slightly, but it does not appear to be certain that the contraction is real. The fact that fused boric acid behaves similarly to more complex glasses is unimportant, unless it is perfectly

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certain that the substance was perfectly pure. Borates, except alkali borates, are very immiscible, and a very small quantity of impurity may be present as a separate phase.

It may be noted that a marked change of volume near the solidifying point was to be looked for as the only way of accounting for the fact that often when two soft glasses of different makes are sealed together they form a perfectly good junction but show a ridge at the point of union. This could not be due to any difference in the rate of contraction over a range outside that at which the glass possessed mobility. Attention may also be called to the fact that if two pieces of glass with optically plane surfaces are placed in contact, and their temperature is raised, there is a definite temperature at which they will become optically united (*Silikat Zeits.*, 1918, III., 213).

These facts point to a very marked discontinuity in the properties of glass in the neighbourhood of the softening point, but they do not furnish any direct evidence in opposition to the idea that glass is a liquid. Within the last week, however, a paper has been published by A. A. Griffiths of the Royal Aircraft establishment (*Phil. Trans.*, A. **221**, 163) which throws some light on the subject.

Working with a glass, of which the composition is given in the paper, having a high softening temperature, he found that at temperatures about 730° the load which a fibre could support was determined solely by the surface tension, which decreased linearly with the temperature. Below 730° a fibre was able to support stress, apart from surface tension, this solid stress increasing from zero at 730° to 1·3 lbs. per sq. in. at 657°, and to 24 lbs. per sq. in. at 540°. The magnitude of these effects is still very small over the whole annealing range.

The most obvious alternative to the suggestion that glass is a liquid, is that it is a colloid, and that with change of temperature it passes through the stages,

$$\text{elastic gel.} \rightleftharpoons \text{colloidal sol} \rightleftharpoons \text{crystalloidal sol.}$$

Looking for some experimental data which would serve as a means of comparing the properties of glass and colloids, I turned to the literature of colloids for information. As Mr. Hatschek has observed in the course of this discussion, no measurements have been made on the thermal and mechanical properties of elastic gels or of the changes which take place in them during gel-sol transformations. Qualitatively there is a distinct resemblance between the changes—

$$\text{elastic gel} \rightleftharpoons \text{sol}$$

and

$$\text{elastic glass} \rightleftharpoons \text{mobile glass.}$$

and I propose to investigate the relationship quantitatively.

The suggestion that glass is a colloid, generally implying some form of a polyphase *liquid* system, though the meaning of the term liquid applied to the phases which make up each system is rather vague, has frequently been put forward. Barus (*Am. J. of Sci.*, 1898, **6**, 270) made use of it to account for the behaviour of glass towards water, and it is indeed difficult to account for apparently erratic behaviour of chemical reagents towards glasses on the supposition that they consist of homogeneous liquid solutions of silica, silicates, &c. (Bibliography, Turner, *J. Soc. Glass Tech.*, I., 1917, 213).

Quincke (*Ann. der Physik*, 1915, IV., **46**, 1025) has put forward the suggestion that glass is a jelly-like structure built up of invisible foam walls separating foam cells, the wall and cell contents consisting

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of a series of liquid phases each containing several modifications of silicic acid. The observations on which his ideas are based are interesting. In examining the copper aventurine glass, which contain microscopic crystals of copper in a transparent glass, he found that in some cases the crystals developed in lines of similarly orientated octahedra. In other cases groups of crystals appeared to be distributed over curved or plain surfaces. These observations point to the existence of fibrous or cellular structures in the glass. Fibrous structures play an important part in the formation of some gels, such as those of the soaps.

In conclusion I must call attention to the conclusions arrived at by Griffiths (*loc. cit.*) in his paper, which should be read by those interested in this subject. As the results of experiments on the influence of flaws in the tenacity of glass, he finds that this tenacity suffers rapid diminution accompanied by shrinkage, following rapid cooling from the mobile to elastic conditions. Very fine fibres of glass, rapidly chilled, have a tenacity approximating to the theoretical value, which is many times greater than the ordinary experimental value. He concludes that in the mobile state (at 1,400°) the glass consists of molecules arranged "at random." On cooling rapidly the random arrangement momentarily persists, but with lapse of time the molecules arrange themselves first in chains of limited length, and afterwards in surfaces. During slow cooling the chain formation takes place most rapidly over the range T_bT_a. The orientation has some relation to the form of the solid produced, accounting for the tendency of glass to flake off from the surface on fracture.

In this connection reference may be made to a well-known phenomenon. If a cut is made round the inner circumference of a glass tube or vessel, as the inner surface is always in tension, owing to the slower rate of cooling, the cut will always extend towards the outside of the tube or vessel, and if it does not do so spontaneously, it will do so on warming the outside. It often happens, however, that when the cut appears to have penetrated to the outside around the whole circumference, a "skin" still remains on the outside which can only be broken by tapping the glass, and even then does not always break through readily or exactly along the line of the cut. At a very small distance from the inner surface the line of fracture bends sharply, becoming parallel with the surface of the glass, so that a thin flake of glass is left projecting from one or other of the several portions. It is frequently stated in chemical literature that the outer layer of a glass article differs from the mass of the glass; but whether it does so in freshly made articles, or only after weathering, is doubtful. The phenomenon referred to above can be observed in any article taken direct from the kiln or lehr, and is probably purely physical in character.

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DISCUSSION

Dr. M. W. Travers (*communicated*) :

I fear that the science of glass-making in this, as in other branches, suffers from too much speculation based upon insufficient experimental evidence. Only one series of experimental researches on the coloured glasses, which may be considered to be homogeneous in distinction from the glasses of the gold-ruby type, in which the effect of a range of colouring materials on a range of typical glasses was studied has ever been carried out. I refer to Zsigmondy's work (*Ann. der Physik*, 1901, IV. 4, 60); but of the 90 possible combinations of colouring materials and glasses, he actually examined very few, and only in a few cases did he vary the concentration of the colouring matter in the glass. Other spasmodic investigations have not increased our systematic knowledge of the subject.

I cannot see that any deep mystery attaches to the cobalt and copper glasses which from the results of Zsigmundy (*loc. cit.*) and of Holt and Burgess (*Eng. Ceramic Soc.*, 1905–6, 163), behave similarly to aqueous solution. Cobalt oxide colours boric oxide glass a faint pink, being very insoluble in the glass. The addition of alkali to the boric acid increases the solubility of the cobalt oxide in proportion to the alkali content, and the glass is now blue. Taken with the fact that the boric oxide glass is an electrolyte, and looking at the problem in the light of researches in aqueous solution of cobalt compounds, are we not justified in assuming that the pink and blue colours are due to simple and complex ions? The same remarks apply to green and blue copper glasses; but while the absorption of light by aqueous solution of copper salts has been carefully studied, our knowledge of the glasses is merely qualitative.

The chemistry of the copper ruby glasses has been investigated by Auger (*Compt. Rend*, 1907, 144, 422), who worked on copper aventurine glass, and found that the separation of copper was due to changes in the equilibrium

$$Cu_2SiO_3 \rightleftharpoons Cu + CuSiO_3$$

The separation of copper can, of course, only take place in a glass free from oxidizing agents and dissolved oxygen. Quantitative investigation might show that similar changes took place in the deposition of gold and other elements in a finely-dispersed state in glass.

Sir H. Jackson's statement on water in the batch—its influence on the subsequent devitrification of the glass—must be limited to certain kinds of glass, and detailed information would be of interest. Formerly all flint glass makers used crystallised potash (12 to 18 per cent. water) in their batch, on account of its freedom from sulphates and chlorides, without ill effects.

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SECTION IV.—NON-AQUEOUS COLLOIDAL SYSTEMS

Sir Robert Robertson, K.B.E., opened the Evening Session, over which Professor F. G. DONNAN, C.B.E., F.R.S., presided, with discussion on "Non-Aqueous Colloidal Systems with Special Reference to Nitrocellulose."

NITROCELLULOSE

BY

SIR R. ROBERTSON, K.B.E., F.R.S.

INTRODUCTION

The principal applications of nitrocellulose in industry are to celluloid, propellants, artificial silk, collodion and some blasting explosives. In this paper I shall confine myself for the most part to nitrocellulose as used in the manufacture of propellants, and I propose to describe some of the relations that exist between the solutions of cellulose and of nitrocellulose and the gelatinised nitrocellulose after the solvent has been eliminated, together with some work on the characteristics of its solutions.

Most of the modern propellants are colloidal in character, and it is to the nitrocellulose which they contain that this character is to be attributed. As they have no definite crystalline structure, and can be obtained as uniform non-porous masses by the process of incorporation or malaxation during manufacture, they present an unbroken surface to the flame which ignites them, and even under pressure continue to burn regularly from layer to layer. It is this property that has enabled guns to be designed much lighter in weight than for gunpowder, and that has made it possible by suitable choice of thickness of the propellant to secure very high velocities of projectiles (within a narrow margin of a few feet per second from round to round) without undue strain on the gun.

To obtain the degree of regularity in ballistics necessary for accurate shooting it is important for the dimensions of the finished propellant to be within very narrow limits. It has been found that the nature of the nitrocellulose used affects the amount of shrinkage which takes place in the cord after squirting from the die, and it is obvious therefore that the colloidal properties of nitrocellulose gelatinised by means of solvents, either volatile or non-volatile, are of great importance in the study of propellants.

I propose to bring to your attention the results of some work on gelatinised nitrocellulose that has been carried out at the Royal Gunpowder Factory, and the Research Department, Woolwich.

Among the more important aspects that have to be considered are the influence on the product of the nature of the raw material, the influence of the process which it undergoes in being nitrated and stabilised by boiling with water, and the effect of these on the characteristics of the finished material. Among other important properties the viscosity of solutions of cellulose and of nitrocellulose in relation to these aspects clearly required investigation.

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Treatments which affect the Viscosity of Cellulose and Nitrocellulose Solutions

In general, those treatments which would be expected to effect disruption of molecular aggregates (*e.g.*, by grinding or chemical decomposition such as hydrolysis) are found to lower the viscosity both of cellulose and nitrocellulose solutions.

The treatment of the cellulose before solution, with bleaching powder (oxidation) or caustic soda (hydrolysis) in the usual processes of cleaning, reduces the viscosity of its solution in cuprammonium. The viscosity of the solution itself is reduced by exposure to air or light, or even to some extent by simply allowing it to stand for some time. The viscosity of the solution of the corresponding nitrocellulose is found to be affected in the same direction.

With the nitrocellulose, the steam boiling treatments given in the purification process lower its viscosity, but there appears to be a practical limit to the process. When the more easily attacked forms of nitrocelloluse have all been destroyed by boiling, the further reduction in viscosity is very slow, and if the cellulose before nitration has been treated so as to reduce its viscosity markedly, no great reduction of viscosity is produced by boiling the nitrocellulose.

In order to produce a nitrocellulose of low viscosity, it is found to be better to reduce the viscosity of the cellulose as far as possible by suitable treatments than to rely on the reduction during boiling of the nitrated product.

It may be mentioned parenthetically on the question of the measurement of the state of molecular aggregation of nitrocellulose in solution, that in a recent paper by Duclaux and Wollman (*Bull. Soc. Chim.*, 1920, **27**, 420), emanating from the Pasteur Institute, while the lower limits of molecular weight of nitrocellulose solutions are shown by measurements of osmotic pressure to be very high, the molecular weight of products of different degrees of viscosity varied from aggregates of 80 times the C_6 formula for cellulose to 270 times in the case of the more viscous samples.

Relation of Viscosity of Solution and of its Nature to the Toughness of the dried Nitrocellulose Colloid

In some earlier work the viscosity was measured by means of a viscosimeter of a simple type, and the toughness of the resulting gelatinised dried nitrocellulose in the form of cord was evaluated by determining the least radius of curvature to which the cord could be bent. This method brought out such differences as that a cord of nitrocellulose of 13 per cent. nitrogen content cracked at a radius of curvature of 100 millimetres when acetone had been the solvent, while a cord of nitrocellulose of 12·4 per cent. of nitrogen broke at a radius of 25 mm. again with acetone as the solvent, and at 5 mm. when ether-alcohol had been used to gelatinise it.

From the results of these experiments it was deduced that when the same simple solvent (acetone) was used to gelatinise nitrocelluloses of a high nitrogen content (13 per cent.) the viscosity of the nitrocellulose solution was inversely proportional to the toughness of the resulting cord. The coherence of the dried nitrocellulose was thus found to be adversely affected by the higher state of aggregation of the molecules of the nitrocellulose, as indicated by the viscosity of its solution. This short note on these experiments has been given, as

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they illustrate a connection between the viscosity of a solution and the physical consistency of the dried nitrocellulose.

The nature of the volatile solvent also affects the brittleness of the dried gelatinised substance. Thus the dried product made by gelatinising nitrocellulose of 12·4 per cent. nitrogen with ether-alcohol is much tougher than that gelatinised with acetone, and a similar effect is obtained by adding some alcohol to the solvent acetone. Caution has, however, to be observed in this connection, as retention of the solvent in an imperfectly dried substance may give a quite fictitious semblance of toughness to a film of gelatinised nitrocellulose. Thus when films of nitrocellulose of 13 per cent. nitrogen are made with acetone and with amyl acetate respectively, clear acetone films of about 0·5 mm. in thickness (and these can be made by taking precautions to prevent access of water vapour during evaporation of the solvent) seem to be much more brittle than similar films made with amyl acetate. When, however, the latter are dried out so that all the solvent, in this case of considerably higher boiling point than acetone, is eliminated, the film is quite as brittle as that in which acetone is the solvent.

Processes for Determining the Viscosity of Cellulose and of Nitrocellulose Solutions

It might now be well to refer to some of the methods that have more recently been found most suitable for determining the viscosity of solutions of cellulose and nitrocellulose, and to state briefly the information that study of this property has afforded. Of great importance in this connection has been the application of the falling sphere viscosimeter (*see* Gibson and Jacobs, *J. Chem. Soc.*, 1920, **117**, 472) in which the velocity is observed, under standardised conditions, of a steel ball, 0·15 cm. in diameter, falling through the solution, appropriate corrections being made for deviations from Stokes' law on account of the side-effect of the walls and the end-effect of the bottom of the viscosimeter tube. This instrument has had a wide application in the study of solutions of nitrocellulose, and the difficulties inherent in its application to solutions of cellulose in cuprammonium solution, chiefly on account of the need for eliminating air in this estimation, have been overcome (Gibson, Spencer, and McCall, *J. Chem. Soc.*, 1920, **117**, 484).

For cellulose dissolved in cuprammonium solution a capillary viscosimeter in which the solution comes into contact only with hydrogen was developed, and the conditions were obtained for the preparation of the cuprammonium solution by a process which gave more reliable results than those described by Ost. By the use of this capillary viscosimeter it is possible to obtain viscosities of more mobile solutions of cellulose in cuprammonium solution than with the falling sphere viscosimeter, for example, below 10 C.G.S. units.

Relation between Viscosity of Nitrocellulose Solution and Cohesion of dried Nitrocellulose Mixtures

Reference has been made to a case in which the brittleness of dried gelatinised nitrocellulose was affected by the nature of the original nitrocellulose and associated with high viscosity of the nitrocellulose solution. A similar relationship came to light when a new nitrocellulose-nitroglycerine propellant (R.D.B. Cordite) requiring ether-

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alcohol as a solvent was used in quantity during the war, in place of cordite M.D. for which the supply of acetone was insufficient. It was found on pressing the incorporated gelatinised material that the extruded cord exhibited a lack of cohesion and of uniformity in diameter which gave rise to difficulties. An investigation of the nitrocellulose and of the cellulose from which it was made was carried out by the application of the processes mentioned above, and ultimately the cellulose was controlled by the falling sphere viscosimeter. By this means the uniformity of the cellulose was ensured, and a limit imposed on its viscosity. It appeared that the lack of uniformity of the pressed cords of this propellant in this case also was due to an unduly high viscosity of the nitrocellulose, and when measures were taken to control the viscosity of the cellulose itself, no further trouble was experienced.

From a consideration of these two examples, one of gelatinised nitrocellulose and the other of a nitrocellulose-nitroglycerine mixture, it would appear that a high state of aggregation of the molecules of nitrocellulose is not conducive to the toughness that is desirable in a product that has to be handled both during manufacture and after.

The subject of the viscosity of cellulose and of solutions of cellulose was further pursued at the Research Department, Woolwich, by the application of the methods of determining viscosity mentioned above, and some of the results obtained in these investigations may now be considered.

Viscosity of Cellulose Solutions and their Relation to Nitrocellulose Solutions

In the first place, as regards the cellulose itself, the reduction in its viscosity brought about by increase in temperature of the alkaline pressure boiling to which the cotton is subjected, and the influence of increase in the concentration of the caustic alkali in this process in the same direction have been described by Gibson (*l.c.*, *p.* 481).

Correlations were then made between the viscosity of the cellulose in cuprammonium solution and that of the solution in ether-alcohol of the nitrocellulose made from it, and it was established that although the processes of nitration and stabilising by boiling of the nitrocellulose tended to level down differences, yet there is a general relationship in the sense of higher viscosity of the nitrocellulose made from cellulose of high viscosity, and it was brought out that if the cotton had been incompletely reduced in viscosity by the soda boiling the viscosity of the finally purified nitrocellulose was with greater difficulty brought down by the steaming during stabilisation.

Minimum Viscosity of Nitrocellulose Solutions

The viscosity of solutions of nitrocellulose in ether-alcohol was then studied (*see* Gibson and McCall, *J. Soc. Chem. Ind.*, 1920, **39**, 172, T) by the method of the falling sphere viscosimeter, and a suspicion that a small change in the proportion of ether to alcohol affected the viscosity, led to a thorough examination of this variant with ether-alcohol solutions of nitrocellulose of different contents of nitrogen and in different concentrations. It was established that

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there was a minimum viscosity at a certain proportion of ether to alcohol, solutions on either side of the minimum being the more viscous, and indeed formed jellies with the higher proportions of either alcohol or ether. The position of this minimum was also found to be independent of concentration, leading to the deduction that this minimum would give the optimum proportions for the solvent used in the process of gelatinisation in the incorporator where the ratio of solvent to substance is necessarily very much less than is any solution of which the viscosity can be measured by the means spoken of above. It may be said that this was verified in practice.

This position of minimum viscosity was found to vary with nitrogen content among those nitrocelluloses which are soluble in ether-alcohol, more ether being required for those with the higher content of nitrogen, and it was also established that the farther the composition of the solution is removed from the point of minimum viscosity, the longer does it take for equilibrium to set in, the process of gelation continuing in some of the mixtures rich in one constituent for a considerable time. It proved to be of importance from a manufacturing point of view to choose the mixture of minimum viscosity, since with the associated proportion of ether to alcohol on the one hand, gelatinisation proceeds with the greatest rapidity, and on the other hand, as this mixture has the maximum fluidity, with the smallest usage of solvent. The practical application of this principle in supply, the large scale experimental work carried out in this connection and the means taken to secure that a nitrocellulose of easy gelatinising properties was obtained by the controlled treatment of the cotton itself are described by Mr. R. A. Punter.

The alcohol used in the above work was of 92 per cent. strength, and it has been found possible by determining the viscosity of a series of binary mixtures of nitrocellulose in ether and alcohol containing varying proportions of water, to obtain a ternary diagram from which the mixture of ether, alcohol, and water that gives the minimum value of viscosity can be read off.

A similar point of minimum viscosity has been found with acetone-water solutions of nitrocelluloses, and it is of interest that the proportion of water in the acetone thus indicated is one which has long been used in the manufacture, having been chosen from other considerations. The phenomena of the gelation of such mixtures are discussed by Masson (*J. Chem. Soc.*, 1920, **117**, 819). The relation between viscosity and concentration, as is also the case with ether-alcohol solutions, appears to conform to the Arrhenius logarithmic expression, but only over a limited range.

Concluding Remarks

The above work has afforded a great deal of information on the nature of the solution of cellulose and of nitrocellulose and forms the basis for theoretical speculation apart from the bearing it has had on manufacture.

The viscosity of the solutions has been proved to have a direct relation to the properties of the dried colloid from which the solvents have been eliminated by drying. The dried colloid, however, presents difficulties in assessing its physical properties. One method of determining its toughness has been mentioned, and determinations of hardness by the Brinell method, of breaking strain, or of resistance to crushing have been applied, but not so far with much that is

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informative. One method may be mentioned by means of which variations in the viscosity of the hard colloid may be traced. If large cords be pressed from different composition of the cordite type in which the proportion of guncotton to nitroglycerine is varied, these cords retain a small proportion of the volatile solvent. If now the quantity of this solvent be determined in different concentric zones it is found that as the nitrocellulose becomes dominant, a proportion is reached when the distribution of the volatile matter is no longer uniform but increases regularly from skin to core, the ratio of the content of volatile matter in the different regions remaining constant although the total quantity is reduced in the process of drying. This resistance to the migration of the solvent is some measure of the viscosity of the horny substance, and its regional determination might, perhaps, assist in the investigation of the physical condition of other hard colloids.

It is hoped that the above will show the importance of the application of the investigation of the colloid solutions of nitrocellulose and indicate, perhaps, points of theoretical interest that remain to be followed up.

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*THE VISCOSITY OF SOME CELLULOSE ACETATE SOLUTIONS

BY

GUY BARR, B.A., D.Sc., AND L. L. BIRCUMSHAW

Summary.—Experiments are described which were made to investigate the changes in viscosity and density of cellulose acetate solutions in acetone on the addition of varying quantities of water, alcohol, and benzene.

In the manufacture of non-inflammable dopes used for tautening the fabric on the wings of aeroplanes, the viscosity of the solution of cellulose acetate in the dope solvent not only limits the concentration which it is possible conveniently to employ, but also necessitates the use of an acetate which does not possess the maximum viscosity in acetone solution, *i.e.*, which is more "degraded" and has less film strength than the best acetate that can be manufactured.

It has long been known that the solubility of cellulose acetate in acetone and the viscosity of the solutions is modified considerably by small quanities of water; but accurate determinations of the extent of this influence have been, up to now, lacking. It was, therefore, thought advisable to study the viscosity concentration (*i.e.*, concentration of water) curve for a 5 per cent. solution of a typical acetate in pure acetone up to the point of precipitation of the acetate. Very interesting results were obtained and it was decided to investigate the influence of benzene and ethyl alcohol (other liquids used in the manufacture of dope) in a similar manner.

Materials used and their Purification. — The cellulose acetate used was "Dreyfus" material, obtained from the Royal Aircraft Establishment in 1914.

Acetone.—This was purified by the method described by Werner and Shipsey, *J.C.S.*, 1913, 1255, and the boiling point of the final material was 56°·5 C.

Benzene.—The benzene was purified by freezing and then by fractionation.

Ethyl Alcohol.—This was dried over quick-lime and fractionated.

Method of making Solutions.—The acetate was dried until the weight was constant and rapidly transferred to a weighed and corked tube. The cork was covered with tinfoil to protect it from the action of the liquid. Measured quantities of the acetone and water, benzene, or alcohol were then added, and the weight of each determined. The mixture was shaken thoroughly from time to time until dissolved, and then allowed to settle for at least one week.

Determination of the Densities.—The densities were determined in a small bulb pycnometer (capacity, 16 c.c.) fitted with a cap. The solution was forced from the containing tube into the pycnometer by compressed air, until the latter was fitted to just above the mark. The pycnometer with its contents was then placed in the thermostat

* The work described in this paper was carried out for the Advisory Committee for Aeronautics, to whom the results were communicated in 1919.

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at 25° for 20 to 30 minutes; the solution adjusted to the mark and the pycnometer and its contents weighed.

Owing to the very viscous nature of the solutions this method was not susceptible of any great accuracy, and for this reason the specific gravities at 25° C. were not converted to densities nor corrected for the buoyancy of the air.

The viscosities were determined in an ordinary "U" form of Ostwald viscometer with suitably wide capillary. The solutions were forced by air pressure into the instrument, and the latter placed in the thermostat for 30 minutes, when the time of flow was taken with a stop-watch reading to $\frac{1}{5}$ seconds. The dimensions of the viscometer were such that a pure sucrose solution of density D_4^{25} 1·25225 had a time of flow of $48\frac{2}{5}$ seconds. According to the experiments of Heber Green (*J.C.S.*, Vol. 93, 1908, 2023), this has a viscosity of 0·2040 C.G.S. units.

The thermostat employed was of the Lowry pattern and the temperature could be kept constant to 0°·020.

The results are tabulated below :—

TABLE 1

Acetone-Water Solutions

Per cent. Water.	Mol. per cent. Water.	Density.	Time of Flow (secs.).	d × t.
0·0	0·0	0·8090	325	263
0·64	2·14	0·8106	249	202
1·10	3·66	0·8123	208	169
2·34	7·56	0·8135	155	126
2·46	7·95	0·8169	152	124
2·66	8·53	0·8167	145	118
3·90	12·15	0·8200	131	107
4·98	15·20	0·8249	122	101
6·56	19·35	0·8278	115	95
7·66	22·70	0·8478	138	117
9·50	26·80	0·8364	147	122
14·12	36·68	0·8522	160	136
18·42	43·70	0·8641	197	170
24·02	52·20	0·8803	255	224
29·00	58·70	0·8930	320	286

TABLE 2

Acetone-Benzene Solutions

Per cent. Benzene.	Mol. per cent. Benzene.	Density.	Time of Flow (secs.).	d × t.
1·33	1·05	0·8106	330	266
2·43	1·93	0·8115	363	294
4·95	3·95	0·8117	394	320
9·65	7·73	0·8175	428	350
14·50	11·75	0·8217	500	411
18·70	15·50	0·8278	626	519
24·20	24·20	0·8326	1,015	845
33·10	33·10	0·8414	2,049	1,724

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TABLE 3

Acetone-Ethyl Alcohol Solutions

Per cent. Alcohol.	Mol. per cent. Alcohol.	Density.	Time of Flow (secs.).	d × t.
0·51	0·68	0·8096	329	266
2·59	3·42	0·8097	249	202
5·18	6·16	0·8094	180	146
10·28	13·35	0·8104	180	146
15·74	20·20	0·8123	172	140
20·26	25·42	0·8123	169	137
24·88	31·30	0·8127	165	134
30·22	37·70	0·8128	165	134
37·96	45·60	0·8147	185	151

The next mixture made up after the last one in each of the tables contained from 5 to 10 per cent. more of the added liquid, and in each case caused precipitation of the acetate.

The curves obtained for the three liquids are very different. Thus benzene causes a progressive increase in viscosity with increased percentage of precipitant, whereas water and ethyl alcohol show an initial fairly rapid fall. It is proposed to extend the list of liquids used, and to investigate in more detail the curves in the region of precipitation. Since other types of acetate may be expected to show different phenomena, some of the curves will also be determined for solutions of cellulose acetate of different manufacture and possessing other characteristics; in addition, other concentrations of acetate will be examined.

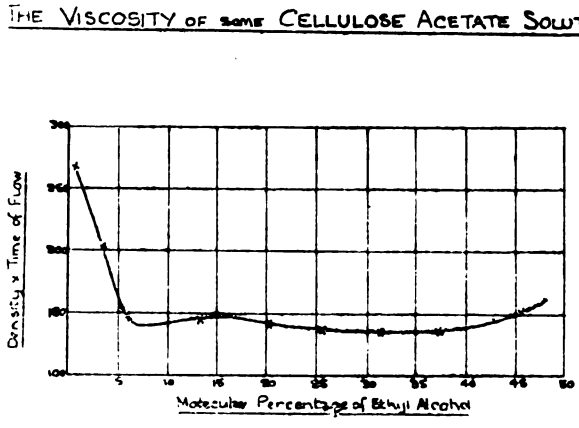

FIG.

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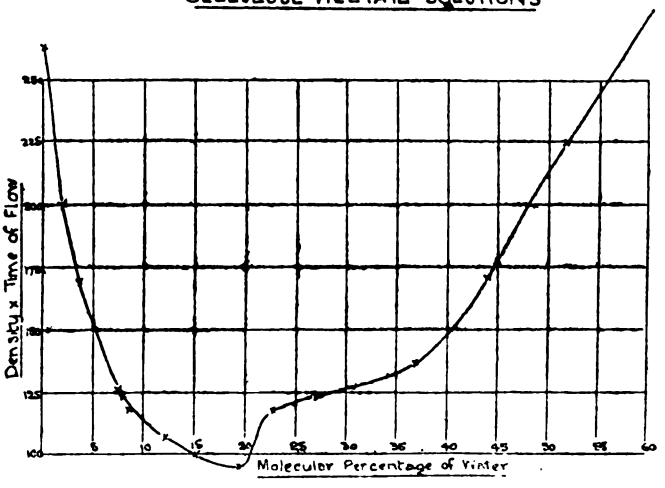

FIG 2

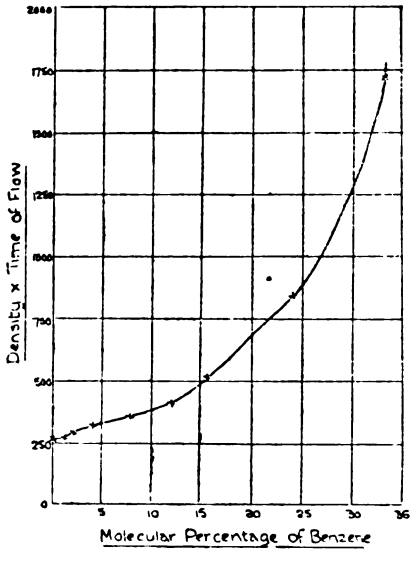

FIG 3

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NON-AQUEOUS COLLOID SYSTEMS WITH SPECIAL REFERENCE TO NITROCELLULOSE

BY

F. SPROXTON, B.Sc., F.I.C.

Nearly all nitrocellulose solvents contain the carbonyl group —CO—in the form of a ketone, ester, or acetyl group. There are, however, some exceptions, and ether-alcohol is one of considerable importance, particularly in view of its extensive use during the war in cordite manufacture. Baker[1] investigated the viscosity of ether-alcohol mixtures and concluded that dissociation of (associated) alcohols takes place in such mixtures, but is accompanied by the formation of an ether-alcohol complex, to which the solubility of nitrocellulose is due. Quite recently, Gibson and McCall[2] have investigated the effect of variations in the proportions of ether and alcohol on the viscosity of ether-alcohol solutions of nitrocellulose. They find that "the optimum solvent for a nitrocellulose depends on its nitrogen content, and that the higher the nitrogen content, the more ether the optimum solvent requires." This method of expressing the result is, perhaps, open to criticism. The composition of the optimum solvent may vary with the nitrogen content, but it may be directly governed by some other factor which usually varies at the same time as the nitrogen content. The variable factors in nitrocellulose are: (1) the structural complexity of the original cellulose; (2) the complexity of the cellulose after nitration; (3) the percentage of nitryl groups; (4) the percentage of free hydroxyl groups; (5) minor functions such as ketonic or aldehydic groups, and sulphuric acid esters. It is possible that the free hydroxyl groups have a considerable influence on the solubility relations. Dry nitrocellulose absorbs moisture from a damp atmosphere. In fact, Will,[3] in 1905, came to the conclusion that the sum of nitrogen percentage plus water absorbed was a constant (14·6). This conclusion was based on the examination of 65 samples of nitrocellulose. Macdonald's observations on the composition of the spent acids from the displacement process[4] are best explained by assuming slight hydrolysis of the nitrocellulose when the nitrating acids are displaced by water. Now, it has been shown by Renker[5] that cellulose dried by alcohol retains traces of alcohol even when dried at 130° C. It is not impossible, therefore, that the free hydroxyl groups in nitrocellulose attract alcohol molecules which would otherwise take part in the formation of the solvent complex, and the variations in the composition of the optimum ether-alcohol solvent for various nitrocelluloses may be due to the differences in the percentage of hydroxyl groups which the nitrocelluloses contain. A simple calculation will show that (1) if Will's generalisation is correct, (2) if the hygroscopicity of nitrocellulose is a measure of its free hydroxyl content, and (3) if the free hydroxyls withdraw alcohol from the ether-alcohol mixture, the results found by Gibson and McCall are *qualitatively* in agreement with the theory that the solvent action of ether-alcohol is due to the formation of a definite ether-alcohol complex. Baker's theory is not, therefore, definitely disproved by Gibson and McCall's observation. Chandelot, in 1912[6], investigated the interesting fact that

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moist nitrocellulose is more soluble in ether-alcohol than dry. Masson and McCall[7] have recently published a paper on the viscosity of nitrocellulose in mixtures of acetone and water, showing that the minimum viscosity is obtained not with dry acetone, but with acetone containing a small percentage of water, varying, for instance, from 8 to 10 per cent. for a sample of nitrocellulose containing 12·3 per cent. of nitrogen, and from 6 to 7 per cent. for a sample containing 13 per cent. of nitrogen. Here, also, there is a suggestion that the free hydroxyl groups of the nitrocellulose modify its solubility relations, and that what really passes into solution is nitrocellulose + water molecules attracted by its free hydroxyl groups. In the case of dilute solutions, *e.g.*, where the concentration of nitrocellulose is about 0·1 per cent., in technically pure acetone (not specially dried), a minimum viscosity is not found as the water content increases. There is a continuous rise to a maximum value and then a fall as the solution is converted to a suspensoid sol. If a minimum occurs, it must be at a lower concentration of water than that normally present in technically pure acetone. It seems probable that in these aqueous-acetone solutions of nitrocellulose we have nitrocellulose present in all degrees of state from emulsoid to suspensoid, and this suggests the question whether it is possible, in the same solution, for emulsoid nitrocellulose to act a protecting colloid to suspensoid nitrocellulose. Mardles, Moses and Willstrop[8] note that water, up to 6 per cent., increases the solvent power of acetone for cellulose acetate, and their paper contains a great deal of interesting information about this cellulose ester. One of their methods of investigation involves the determination of "transition temperature," *i.e.*, the temperature at which a non-solvent for cellulose acetate becomes a solvent. Since there are many transition temperatures, this might be called the Tyndall point. If a solvent is diluted by an indifferent non-solvent, such as petrol, the transition temperature is raised, and by extrapolation a value can be found for the transition temperature of the petrol. This value is artificial, because it is frequently far above the decomposition temperature of cellulose acetate, but it is useful as an index of solvent power. In the case of many binary mixtures, it is found that the curve connecting the composition of the mixture with the transition temperature shows a minimum. Such results are, of course, parallel to those obtained for the viscosity of the nitrocellulose in ether-alcohol, and it is interesting to note that the authors find that the minima in the cases of tetrachlorethane and alcohol, butyl formate and alcohol, methyl benzoate and alcohol, approximate very closely to mixtures in simple molecular proportions, which, again, suggests that the solubility is due to the formation of a molecular complex in such mixtures of substances which are themselves non-solvents.

In a contribution to the third British Association Report on Colloid Chemistry, I have mentioned another method of investigating such binary mixtures, which consists in making use of a nitrocellulose of incomplete solubility, and determining the percentage dissolved by various mixtures of the liquids under examination. Alcohol and toluene show a maximum solvent power for the samples of nitrocellulose tested, at a concentration corresponding closely to three molecules of alcohol to one molecule of toluene. The toluene and acetone solubility curve shows no maximum, the solvent power of the mixture decreasing continuously as the percentage of toluene increases. The addition of a constant percentage of petroleum spirit

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to alcohol and toluene does not appear to alter the position of the optimum ratio of alcohol to toluene, but reduces the solvent power throughout the curve. The same method has been applied to investigate the solvent powers of mixtures of alcohol and tetrachlorethane for acetyl cellulose. Almost complete solubility has been obtained in mixtures containing between 20 and 60 per cent. of alcohol. It should be observed that this method is not nearly so sensitive as the viscosity method, and less sensitive than the transition temperature method of studying solvent power, but it has some technical advantages. To sum up, the solvent power for cellulose esters can be studied by the following methods :—

(1) Viscosity determinations, the assumption being that that solvent is the best which gives solutions of lowest viscosity.

(2) Determination of transition temperature, *i.e.*, the temperature at which a liquid or mixture of liquids becomes a solvent.

(3) Determination of the amount of an indifferent diluent which may be added to a solution before precipitation takes place.

(4) Determination of the amount dissolved from a sample of cellulose ester of incomplete solubility.

It would be premature to say whether these four methods all lead to the same result, but I have not found any contradictory results up to the present.

Duclaux and Wollman,[9] by the fractional precipitation of an acetone-solution of nitrocellulose by means of water or aqueous acetone, have separated it into fractions of widely different viscosities, although of constant nitrogen content. Since the treatment is equivalent to treating nitrocellulose with aqueous acetone of varying water content, presumably the latter treatment would also fractionate nitrocellulose in this way, and it may be that method (4), given above, has this effect. With regard to the actual peptisation of nitrocellulose, there is little to add to Bancroft's report in the second British Association Report. Masson and McCall,[7] commenting on the variations of viscosity with time in the case of solutions of nitrocellulose in ether-alcohol and in acetone, remark that two processes appear to be at work : (1) the absorption of solvent by nitrocellulose, accompanied by dispersion of the resulting gel; (2) a change in the already dispersed gel, perhaps in the state of aggregation, not necessariy accompanied by alteration in percentage composition. I have occasionally noticed evidence of the two phenomena mentioned in (1) when preparing nitrocellulose solutions. If, for instance, celloidin (a special form of nitrocellulose in small cubes) is covered with a mixture of 80 per cent. alcohol and 20 per cent. acetone and allowed to stand, after a few days one sometimes notices the formation of two boundaries. The lower one, which is separated from the core of still unswollen nitrocellulose in the centre of the cubes, is usually undulating (corresponding to the original surface of the solid celloidin), and is sharply marked by a difference in refractive index from the supernatant liquid. A few millimetres above this will be seen a horizontal layer, often marked by a layer of fine dust which has fallen through the solvent and been stopped by the slowly-diffusing viscous solution. The lower layer is evidently the boundary of the swollen gel, the upper layer the limit of the dispersion process. The fact that the upper layer is horizontal shows that the viscosity of this phase is low enough to allow relative motion in the liquid.

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The colloid chemistry of the manufacture of solid celluloid is complicated and difficult. Contrary to a somewhat widespread belief, at no stage of the manufacture do we deal with a sol, if we except a momentary formation at the surface of the fibrous nitrocellulose when the liquid solvent first comes into contact with it. The amount of liquid solvent employed is less than the nitrocellulose would take up in its preliminary swelling if soaked in the solvent. As a matter of interest the volume of the gel formed under these conditions depends on the concentration of the camphor solution. For example, samples of the same nitrocellulose soaked in alcoholic solutions of camphor of 20 per cent., 30 per cent., and 40 per cent. concentration gave gels in which the specific volume of the nitrocellulose was 4·4, 3·8, and 3·5 respectively.

Since the product of preliminary swelling is a gel, it follows that the whole of the manufacture of solid celluloid from nitrocellulose deals with the gradual transformation of a gel to a solid. This transformation is accomplished by loss of solvent, which involves loss in weight and in volume, while undoubtedly the mechanical properties of the finished material are influenced also by the amount and character of the manipulation it receives in the plastic state. I have given in the British Association Report some information about the ratio loss of weight/loss of volume in the seasoning process. Since the range of density of all possible solutions of alcohol and camphor at ordinary temperatures is very small, it is interesting to find that the value of the ratio falls within this range. In the seasoning process, the loss of solvent is rapid at first, but a skin of harder and denser celluloid forms on the surface, and seasoning becomes progressively slower as this skin increases in thickness. With moderately thick sheets (*e.g.*, 1 cm. and over) even after the loss of weight has become inappreciable, the centre of the celluloid is softer than the outside, and this fact must be taken account of in any investigation of elasticity, since the usual mathematical theory assumes homogeneity of the material. If a rectangular prism of moderately thick seasoned celluloid is sliced down the middle, each piece will assume a curve with the new surface concave, owing to the escape of solvent and consequent shrinkage. A cube of celluloid of 3-in. side made many years ago, and now in use as a paper-weight, shows a lens-shaped bubble inside where the soft core has gradually shrunk away from the hard outer shell. The final material is usually regarded as a solid solution of camphor and nitrocellulose, but the traces of alcohol which are retained probably form an integral part of the system. The reasons for the plasticity of celluloid when warm (one of its most valuable properties) lead to interesting speculations. Nitrocellulose has no melting point, since it decomposes before this point is reached. Camphor melts at 182·5° C. Celluloid becomes appreciably plastic at 80° C. Therefore the melting point, if the term may be allowed, of the mixture is greatly below that of either constituent. The traces of alcohol present no doubt have a considerable influence in reducing the melting point further than would be the case with camphor and nitrocellulose alone. It may be noted in passing that camphor forms liquid mixtures with several solid substances at ordinary temperatures, and possibly this is one of the properties which make camphor adaptable for celluloid manufacture. Most of the substances which have from time to time been used as camphor substitutes have had much lower melting points than camphor, but the celluloid made from them does not usually become

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plastic at a lower temperature on that account. It would appear, therefore, that the plasticity of warm celluloid is determined not by the melting point of the solid solvent, but by the properties of the complex solid solution formed by nitrocellulose, solid solvent, and liquid solvent. When experimenting with unusual materials, one sometimes encounters limits to the mutual solubility, and the phenomenon occurs known in the industry as " exudation." Mardles, Moses, and Willstrop[8] mention occasional cases of crystallisation on acetyl cellulose films. This separation of the solid solvent no doubt depends on its solubility in the liquid solvent and in the nitrocellulose, and it would be an interesting phase rule study, although of great experimental difficulty. I have not seen it occur with camphor, probably because of (1) the high mutual solubility of camphor, nitrocellulose, and alcohol; (2) the high vapour pressure of camphor, at ordinary temperatures, which would cause the camphor to volatilise immediately. Probably it could be tracked in the case of camphor by searching for a break in the seasoning process, using a sample of unusually high camphor content.

References

[1] Baker, *Trans.*, 1913, 653.
[2] Gibson and McCall, *J.S.C.I.*, 1920, **39**, 172T–176T.
[3] Will, *Mitt. Centralst. f. Wiss. Tech. Unters*, Berlin, 1904, No. 4, 1–33.
[4] Macdonald, *J.S.C.I.*, 1911, **30**, 251.
[5] Renker, " Ueber Bestimmungsmethoden der Cellulose " (Berlin University, 1909; *Analyst*, 1910, 35, 71).
[6] Chandelon, *Bull. Soc. Chim. Belg.*, 1912, 26, 495–506.
[7] Masson and McCall, *Trans.*, 1920, **117**, 819–823.
[8] Mardles, Moses and Willstrop; Advisory Committee for Aeronautics; Reports and Memoranda, No. 568.
[9] Duclaux and Wollman, *Bull. Soc. Chim.*, 1920, **27**, 414–420.

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THE ACTION OF LIGHT AND OXYGEN ON RUBBER

BY

B. D. PORRITT, M.Sc., F.I.C.

The prejudicial effects of light on rubber, technically known as "perishing," attracted the attention of Thomas Hancock nearly 100 years ago, and as a result of experiments, he found that by blackening the surface of the rubber, deterioration could be prevented ("Origin and Progress of the India Rubber Manufacture," London, 1857, p. 29). The deleterious effect on the rubber proofing of certain dressings present in dyed fabrics—presumably metallic mordants—was remarked, as also was the fact that the non-caoutchouc constituents of the rubber exercised a marked protective influence (*ibid.*, p. 32).

With the introduction of the telegraph some 30 years later, and the employment of gutta percha for insulating purposes, attention again was directed to the subject owing to the numerous cable failures which initially occurred, and a Joint Committee of the Privy Council for Trade and the Atlantic Telegraph Co. was appointed to report on the matter.

As a result of investigations carried out at the instigation of this Committee and the Director of Indian Telegraphs, it was found that (W. A. Miller, *J. Chem. Soc.*, 1865, **18**, p. 273; A. W. Hofmann, *J. Chem. Soc.*, 1860, **13**, p. 87) the alteration took place only on exposure to air and light when an alcohol soluble oxidation compound, termed in the case of rubber "Spiller resin" (J. Spiller, *J. Chem. Soc.*, 1865, **3**, p. 44) was formed. It was further suspected that this change was promoted by contact with copper (*see* W. Thomson and F. Lewis, *Proc. Manchester Lit. and Phil. Soc.* (4) **4**, April 1891). No further material contribution was made to the subject until recent years, when the question of "tackiness" in raw rubber began to receive attention. It was found by D. Spence (*Quarter Century No. I.R.J.*, 1909, p. 43) that while "tacky" rubber was characterised by possessing a low solution viscosity compared with the normal material, no difference could be detected in chemical composition; while E. Fickendey (*J. Chem. Ind. Kolloids*, 1911, **9**, p. 81), by exposing rubber to sunlight in tubes containing air and other gases, proved that the presence of oxygen was necessary before this defect could develop. These two important observations were later confirmed by A. Van Rossem (*Rubber Industry*, 1914, p. 149) and K. Gorter (*Le Caoutchouc et la Gutta Percha*, 1915, **12**, 8,724).

In 1906 an attempt by Herbst (*Ber.*, 1906, **39**, p. 523) to determine the composition of the products formed by the action of air on a hot solution of rubber in benzene resulted in the preparation of three different substances, one a viscid syrup constituting the main product, having a composition approximating to $C_{10}H_{16}O$, and the other two resinous compounds with a higher oxygen content corresponding to $C_{10}H_{16}O_3$, one being an amorphous powder and the other a brittle solid. Passing reference might also be made to the important work of C. Harries on the products formed by the action of ozone on rubber.

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Hitherto no attempt appears to have been made to study the progress of the oxidation of rubber by any accurate quantitative method, and it was left to Peachey in 1912 (*J.S.C.I.*, 1912, p. 1103) to supply this omission.

By determining the rate of absorption of oxygen by a thin film of rubber deposited on the interior surface of a flask heated to 80° C., it was shown that initially little chemical change took place, a period of rapid oxidation then set in, slowly diminishing as the reaction neared completion, when the amount of oxygen taken up corresponded with the formula $C_{10}H_{16}O_4$. The removal of resin was found to considerably hasten the start of the reaction.

It was pointed out by Wo. Ostwald (*J.S.C.I.*, 1913, p. 179) that the graph obtained by plotting Peachey's results was of the type characterisitic of autocatalytic reactions—an analogy which is supported by the suspicion that traces of peroxides are formed during the process of oxidation.

In a further communication (*J.C.S.I.*, 1918, 55T), Peachey and Leon showed that the removal of moisture exerted no effect on the rate of oxidation, that balata differed from rubber both in regard to the rate of the reaction and in the final product containing a higher proportion of oxygen, and they further demonstrated that a proportion of CO_2 was formed during the reaction at the somewhat elevated temperature employed. In connection with this last observation, it is surprising that none of the published investigations dealing with the perishing of rubber contains any reference to the pungent acid odour which, under ordinary conditions, is a well-marked feature of the change equally with rubber, gutta percha, and balata. (See, however, H. P. Stevens, *J.S.C.I.*, 1919, p. 196T.)

We may now, perhaps, turn for a moment from the scientific to the technical aspect of the question, more particularly in connection with the manufacture of balloon fabric, which probably represents one of the earliest uses—apart from erasers—to which rubber was put (*see Mechanics Magazine*, 1836, XXIV., p. 529—The " Coronation " Balloon Lost off Beachy Head, 1822).

It was generally recognised that it was to the ultra-violet region of the spectrum that the deleterious effects of light on rubber must be attributed, and consequently in order to protect material exposed to drastic weathering, some absorbent screen was desirable, as had been shown many years before by Hancock. The methods initially employed were either to dye the outside ply of cotton yellow (Porritt and The North British Rubber Co., Eng. Pat., 1972/1913) or to protect the outer surface with a light layer of rubber pigmented yellow or red.

The use of rubber compounds containing heavy metals such as litharge (Porritt and The North British Rubber Co., Eng. Pat., 11743/1912) or aluminium powder, was also suggested. While these methods of protection were reasonably adequate for the conditions which obtain in temperate climates, they failed to satisfy the demands imposed by the intense radiation experienced in tropical countries, and when, therefore, a call arose during the War for aeronautical equipment for the East, a novel situation had to be faced. Two types of protection have been found to give satisfactory results under such conditions. The one (J. H. Mandleberg and J. Mandleberg & Co., Eng. Pat., 124495/1919) which involves the employment of small proportions of litharge and other ingredients amongst the proofing mixing probably depends mainly on the formation in the

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rubber of lead sulphide in a colloidal form—a phenomenon which has been previously noted (Lewis and Waumsley, *J.S.C.I.*, 1912, p. 518).

The other, which has been termed the "molecular protection process," (Wheatley and The North British Rubber Co., Eng. Pat. 5915/1915) involves the selective absorption of the ultra-violet light by a suitable coloured organic compound actually dissolved in the rubber.

By the use of either of these two methods, especially if combined with some of the earlier protective processes, it is probable that at present the determining factor for the life of a balloon envelope in the tropics is the durability of the textile rather than that of the rubber.

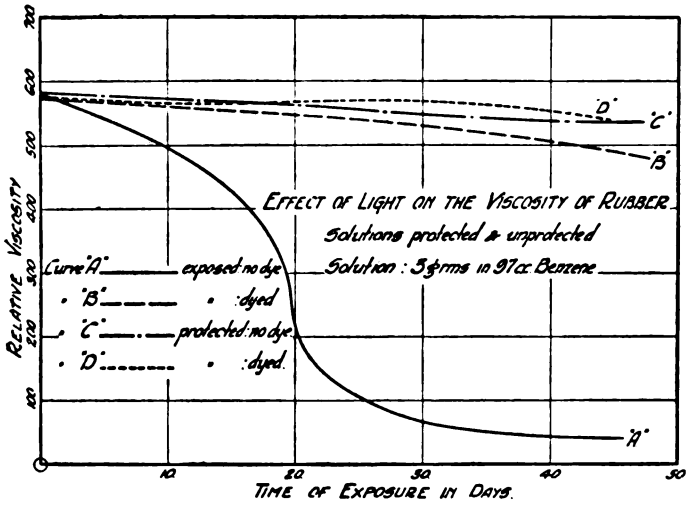
This brief digression may serve as an explanation for, and introduction to some experiments carried out in connection with the second of the two protective processes just described.

As it was known that the viscosity of rubber solutions was rapidly reduced by exposure to light, it was thought that this might afford a more rapid method of judging the protective efficiency of different rubber-soluble colouring matters than the customary balloon fabric outdoor exposure test, which, in a northern climate, is at all times a tedious process, and particularly so during winter months.

As will be evident from the Graph No. 1, which represents the behaviour of a benzene rubber solution with and without Sudan III. (composition : 3 grammes masticated rubber, 0·06 grammes Sudan III., 97 c.c. benzene), the method gives very striking results, indicating that the change of viscosity experienced by rubber solutions exposed to light is to be attributed to that portion of the incident radiation having an oscillation frequency greater than 2,000.

Some preliminary experiments on the absorption spectrum of a specially purified caoutchouc-ether solution made by S. J. Lewis and the writer point to the light absorption in this region being of a general character. (*J.S.C.I.*, 1921, 618 T.)

GRAPH I



That the function of the dye is probably that of a light filter only, and not a catalyst, was shown by exposing to light three bottles

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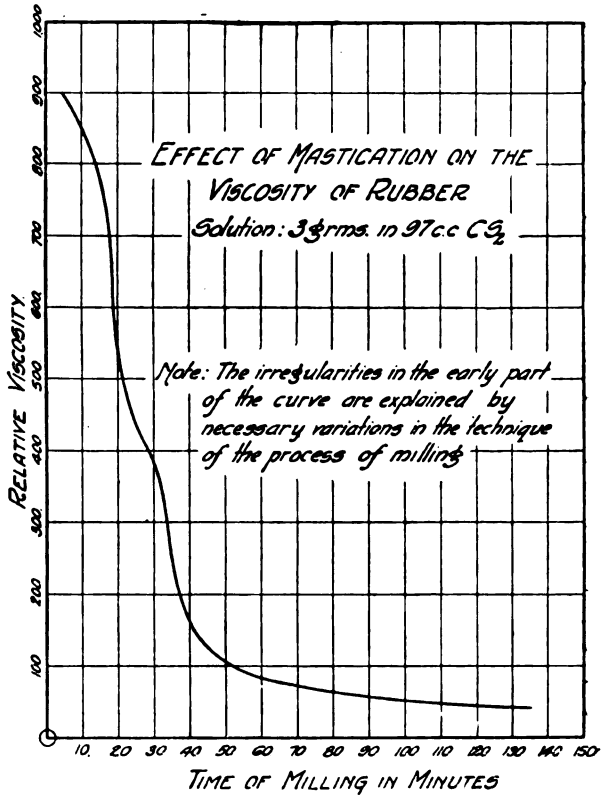
containing rubber solution suspended in jars full of benzene. To the first no dye was added; in the second the solution was coloured by the addition of sudan III., while in the third an equivalent amount of this colour was added to the surrounding benzene. The viscosity changes over a period of two months were as follows :—

	Unprotected.	Protected Internally.	Protected Externally.
Initial Visc. - -	548·7	548·7	548·7
31 days exp. - -	52·5	457·0	473·2
60 days exp. - -	30·2	339·2	393·5

This investigation was subsequently extended in other directions. As is generally known, the process of "mastication," which forms an essential preliminary process in the preparation of rubber for factory use, is also characterised in its initial stages by a remarkable diminution in the solution viscosity of the rubber. This will be evident from the following curve :—

GRAPH II


EFFECT OF MASTICATION ON THE VISCOSITY OF RUBBER
Solution: 3 grms. in 97 c.c. CS_2
Note: The irregularities in the early part of the curve are explained by necessary variations in the technique of the process of milling
RELATIVE VISCOSITY
100
200
300
400
500
600
700
800
900
1000
10. 20 30 40 50 60 70 80 90 100 110 120 130 140 150
TIME OF MILLING IN MINUTES

With a view to determining whether the changes produced by the process of mastication had any effect on the susceptibility of raw rubber to light, a range of samples was obtained throughout the operation, and from these solutions were prepared and exposed, the viscosities being determined at intervals. The results would

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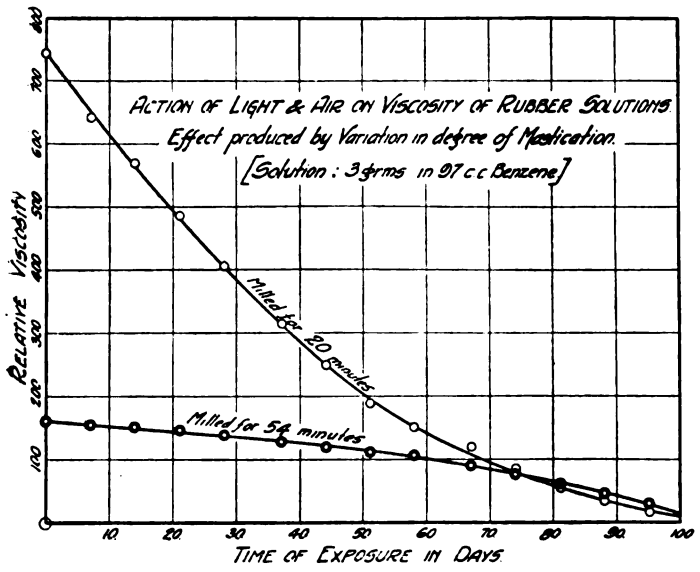
suggest that the physical changes produced in rubber by mastication are not necessarily the same as the initial effects arising from exposure to light and air, and that the stability to light may increase rather than diminish with the severity of the treatment, though this is at variance with the results of Weber, who found that overmilled rubber was prone to oxidation. (C. O. Weber, *I.R.J.*, 1903, **25**, p. 639.)

GRAPH III



In conjunction with the foregoing experiment, a duplicate set of solutions was retained in the dark and tested in non-actinic light. The results, which need not be quoted in detail, showed in most instances little or no change whatever after several months' storage. In the case of the samples of higher viscosity, however, a slight increase was indicated. The behaviour of the rubber itself on keeping in the dark at ordinary temperature was accordingly examined, and some of the results obtained are shown on the following graph (*see next page*).

The remarkable irregularities in the results of the samples of higher viscosity at first gave rise to much speculation, but on investigation it was found that the viscosity of the surface material exposed to air was much lower than that in the interior of such samples, from which it reasonably may be inferred that the presence of oxygen tends to inhibit the "regain" characteristic of under-masticated rubber.

Before making any generalisation regarding the preceding observations, it is desirable to draw attention to the fact that the action of light and air on rubber is not always associated with ill-effects. In the early days of the industry, exposure to sunlight—a process termed "solarisation"—was frequently employed to produce a type of surface vulcanisation (Charles Goodyear, "Gum Elastic," New Haven, 1855, pp. 93 and 113, also Thomas Foster, Eng. Pat. 10092/1844), and this primitive method still appears to be employed

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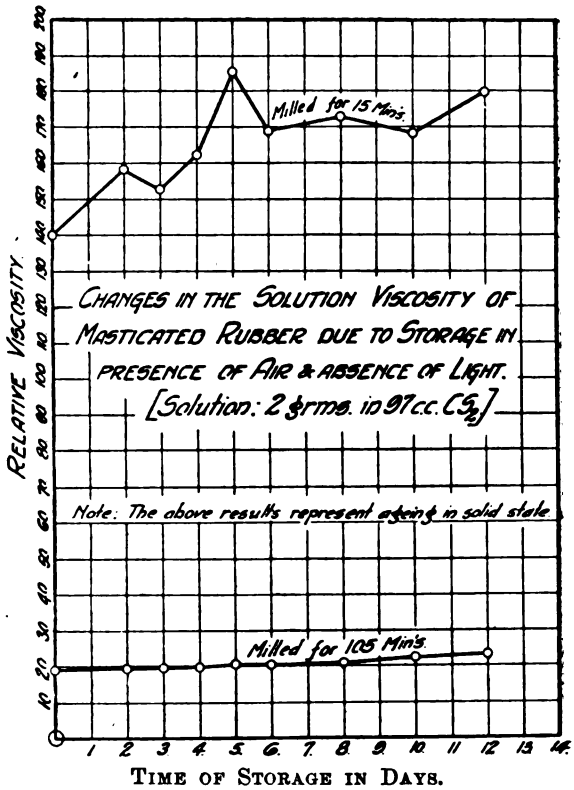
by the native tribes of South America for the production of crude articles for their own use.

A comparatively recent development of this old process involves the use of light sources rich in ultra-violet (Helbronner and Bernstein, *Le Caoutchouc et la Gutta Percha*, 1915, **12**, 8720) for the production of " solutions " of vulcanised rubber, and under the influence of a quartz-mercury vapour lamp, a solution of rubber and sulphur undoubtedly rapidly sets to a stable " gel " accompanied by the combination of a small proportion of the sulphur.

GRAPH IV


RELATIVE VISCOSITY.
Milled for 15 Mins.
CHANGES IN THE SOLUTION VISCOSITY OF MASTICATED RUBBER DUE TO STORAGE IN PRESENCE OF AIR & ABSENCE OF LIGHT.
[Solution: 2 grms. in 97 c.c. CS_2]
Note: The above results represent aging in solid state
Milled for 105 Min's.
1 2 3 4 5 6 7 8 9 10 11 12 13 14

TIME OF STORAGE IN DAYS.

Under ordinary daylight conditions it is found, however, that the addition of sulphur to a rubber solution, if anything, accelerates the rate of viscosity diminution, and it was consequently thought of interest to see whether the removal of oxygen would enable the sulphur to respond to the more feeble, incident radiation. An experiment in this direction did not, however, produce the anticipated result, those solutions to which crystalline sulphur had been added showing no apparent change after several months exposure, while the blank sample containing rubber only, after a few days suddenly set to a " gel " without any obvious preliminary increase in viscosity. This " gel," moreover, on exposure, was found to be rapidly transformed to a liquid.

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It is hoped shortly to design a viscometer which will enable these peculiar changes to be studied more thoroughly, using specially purified materials in view of the marked effects produced by traces of acid (Spence and Kratz, *Z. Chem. Ind. Kolloids*, 1914, **14**, p. 262), and to verify Van Rossem's statement that, even in the absence of air, the action of light results in a reduction in the viscosity of rubber solutions.

While it would appear likely that the presence of air is not favourable to the light vulcanisation effect, it must be noted that in the nascent condition, oxygen is itself capable of producing a similar result, since organic peroxides which have recently been put forward as vulcanising agents (I. I. Ostromisslensky, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1467) have been proved in a measure to function as such (H. P. Stevens, *J.S.C.I.*, 1917, 107).

Finally, it may be of interest to draw attention to the important, but generally unrecognised, effect which is produced in the vulcanisation of rubber by the agency of sulphur and heat when this process is carried out in the presence of air. Those familiar with the early history of the industry may recall the fact that Goodyear's discovery of this remarkable transformation was due to the accidental heating of a piece of rubber containing sulphur and white lead either before or on a hot stove. Hancock, when independently endeavouring to obtain the same result, secured no success by heating samples containing rubber and sulphur alone, and ultimately discovered that to effect the change desired it was necessary to *immerse* the rubber in molten sulphur.

Technical experience has confirmed these early observations and proved that with sulphur only the absence of air is necessary to ensure vulcanisation, while to secure satisfactory results by the "dry heat" process, the use of a positive catalyst such as litharge, in addition to sulphur, is indispensable.

Comparatively little is known regarding the mechanism of the changes which take place during the perishing of vulcanised rubber, beyond the fact that the final products resemble those of raw rubber in properties and composition, that oxidation takes place in the absence of light if the material has been over-vulcanised and is probably promoted by the presence of various catalysts.

Recent work, however, has shown that marked alterations take place on ageing in the tensile properties of over-vulcanised rubber prior to oxidation setting in (*Annual Report on the Progress of Applied Chemistry*, 1919, p. 338), and it is possible that in this preliminary physical change oxygen is again functioning as a catalyst—a suggestion which is now under investigation.

The preceding *résumé* of the information which is available on the effects produced on rubber by light and oxygen acting either together or independently, may be summed up briefly under the following headings :—

(*a*) Under ordinary conditions the action of light and oxygen would appear to take place in two stages, the first being an alteration in the state of the molecular aggregation during which oxygen functions mainly as a catalyst, and the second a series of chemical reactions in which the active participation of oxygen is promoted by the formation of an auto-catalyst—probably a peroxide.

(*b*) The development of the former alteration which constitutes "tackiness" is probably further promoted or retarded by other

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catalysts, while the final transformation into resinous compounds of indefinite composition known as "perishing" is possibly affected by an entirely different set of activating and inhibiting agents.

(*c*) Though the reduction in the solution viscosity which characterises the first effects of light and oxygen on rubber can be reproduced by the application of either heat or mechanical working in the cold, it is doubtful whether the changes thereby produced in the rubber are in other respects analogous.

(*d*) In the presence of sulphur and under the influence of a light source rich in ultra-violet, in place of "depolymerisation," a change resembling vulcanisation is induced.

(*e*) In the absence of air, "tackiness" will not develop in the solid as a result of exposure to daylight, while a benzene-rubber solution under similar conditions sets to a "gel" which liquifies on re-exposure to air.

(*f*) In the absence of actinic light, rubber, either solid or in solution, undergoes no reduction in viscosity as a result of exposure to air, but if previously submitted to a limited amount of mastication, tends to regain its initial properties. This change is, however, partially inhibited by oxygen.

(*g*) The efficiency of sulphur as a vulcanisation agent, unless supplemented by the presence of an appropriate accelerator, is neutralised by the presence of oxygen.

(*h*) Under certain conditions oxygen would appear capable of assuming the function of a vulcanising agent.

In considering the foregoing summary of the work in connection with the changes resulting from the action of oxygen and light on rubber, it will be well to remember that the little which is known is either related to chemical properties or else to one physical characteristic, namely, viscosity.

It is hardly likely that an obviously complex series of changes can be completely elucidated in so simple a manner, and the results of a careful study of other physical properties must be awaited before a definite understanding is reached.

For the moment it will suffice to say that next to sulphur, oxygen is probably the most important rubber catalyst, and that its effects must be carefully considered at all stages from the photo or bio-synthesis of caoutchouc in the latex to the final transformation of rubber into a manufactured product.

In conclusion, the writer has to express his obligation to the North British Rubber Co., Ltd., for their permission to make use of some results obtained in the course of work carried out in their research laboratory.

British Rubber and Tyre Manufacturers' Research Association,
Chemistry Department,
University College,
London.

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The following contribution to this section of the Discussion was received from **Professor Dr. Wolfgang Ostwald** (Leipzig) in response to an invitation :—

CONTRIBUTION TO THE DISPERSOID ANALYSIS OF NON-AQUEOUS SYSTEMS

BY

WOLFGANG OSTWALD (Leipzig)

1. *Introduction.*—Although the study of non-aqueous dispersoids is of well-recognised importance, especially in technical respect—as is proved by the selection of the subject as one of the problems for this discussion—there are only a few researches on certain dispersoid-chemical characteristics of such systems. Solutions of nitrocellulose, *e.g.*, are usually spoken of as colloidal. De Mosenthal[1] has, indeed, found that nitrocellulose solutions in acetone do not dialyse through pig's bladder and parchment paper, and that they do not exert any "osmotic" pressure. On the other hand, J. Duclaux and E. Wollman[2] observe distinct "osmotic" pressures and at least partial dialysis when using membranes of denitrated collodion. Still less accurate is, for instance, our knowledge of the degree of dispersions in solutions of resins, fats, oils, dyes, &c., in organic dispersion media. *Indirectly* we conclude sometimes that such systems are colloidal in nature because of the marked viscosity-concentration function, the formation of jellies or the phenomena of swelling. An exact characterisation by the classical methods of diffusion or dialysis is almost always missing, however.

The main reason for the want of such researches lies presumably in our methods. We may not, without restrictions, apply to non-aqueous systems the methods worked out for aqueous dispersoids, nor the membranes used. If we study the dialysis of acetone solutions through parchment paper, *e.g.*, we must first establish that there are, with respect to these membranes, *both* diffusing *and* non-diffusing acetone solutions. An always negative dialytic effect, as well as an always positive effect, would only show that the membrane is either too dense or too permeable for the solvent in question to admit of differentiation according to degrees of dispersity. The point is not only whether the membrane in itself possesses a gel structure; the degree of shrinkage or solvation of the membrane must have suitable mean values in the respective organic solvents.

The following is a small contribution to the methodics of dispersoid analysis for systems, the dispersion medium of which is alcohol of 96 or 97 per cent. The selection of this alcoholic concentration is not arbitrary, but the result of practical experience with alcoholic media of various concentrations. This concentration has proved to yield much more stable and more easily reproducible relations than alcohol of higher strength; the concentration is particularly interesting also in technical respect. Experiments with other dispersion media will be published on another occasion. Many years ago the author conducted experiments, not yet published, on dialysers for organosols. The experiments described in this communication are new and were made by the author in conjunction with Dr. P. Wolski.

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2. *Preparation of a Stable Alcosol for Purposes of Control.*—It is very easy, it will be seen, to prepare molecularly-dispersed, *i.e.*, dialysing and diffusing alcoholic solutions, but not easy to prepare stable alcosols. On the other hand, the possibility of preparing a tolerably stable alcosol as standard liquid is presumed for the experiments to be described. Of the various alcosols tried, (Ag, $Fe(OH)_3$, As_2S_3, &c.) the *mercury sulphide alcosol*, previously prepared by A. Lottersmoser, proved most suitable. We start from a solution of any concentration, including the saturated (10 per cent.) solution, of mercury cyanide $Hg(CN)_2$ in alcohol of 97 per cent. (*not* stronger). A brisk current of H_2S is passed through this solution for a considerable time, say, 10 minutes. Any flakes, occasionally noticed, will be peptised again on further treatment with H_2S. A sol of dark deep-brown colour is formed; it may be diluted with alcohol of 97 per cent. and then be stabilised by further treatment with H_2S. In a closed vessel the sol may be kept for weeks; a certain excess of H_2S seems to favour stability.

The *freshly*-prepared sol, containing H_2S, may be diluted with the same volume of ether without showing any precipitate after two days. This is important for some of the experiments.

As a typical molecularly-dispersed system in alcohol of 97 per cent. *Night Blue* may be recommended, which is known as a typical colloid in water. The following arrangements for dialysis and diffusion are best tested with the mercury sulphide alcosol on the one hand, and alcoholic night blue on the other.

3. *Dialysers for Alcosols.*—Among the membranes which admit of dialytic differentiation of dispersoids in alcohol of 97 per cent. are the following :—

(*a*) Common Parchment Paper.

(*b*) Collodion Membranes. These membranes are prepared by the same method which the author recently described for the preparation of analytical dialysers for hydrosols.[3] Extraction bags of paper are impregnated with 97 per cent. alcohol. Pharmaceutical collodion solution of 4 per cent. is poured into the still wet bag; the bag is quickly dried in a warm place, so as to feel dry to the touch of the finger, until the smell of ether has disappeared. The same collodion solution is poured in for the second time and the drying is renewed; the dialysers will then be ready for use.

In making use of the dialysers care should be taken to have the liquid inside and outside at the same levels; excess pressure may render these dialysers—as well as the others to be mentioned—leaky. With long standing some collodion will dissolve in the alcohol; the bags need not lose their tightness for this reason, however.

(*c*) *Rubber Membranes.*—The material used is a thickish ethereal solution of unsmoked crepe as formed when an excess of caoutchouc is kept standing with ether for a long time in the dark. Diluted thinnish solutions of rubber have not given good results. Exactly as with the colloid membranes just mentioned the bags are moistened with alcohol and treated and dried for periods of from 5 to 10 minutes.

(*d*) *Gelatine Membranes.*—The solution used was 1 per cent., aged under thymol. The preparation is as just described, except that the two drying intervals must be prolonged to 24 *hours*.

4. *An Alcoholic Jelly for Diffusion Experiments.*—In demonstrations of dispersoid analysis it is customary to place a layer of the solution to be tested on a suitable jelly. Especially when the systems are

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coloured, it is easy rapidly to distinguish colloidal from molecularly-dispersed systems either by the penetrations of the solution into the jelly, or by the observation that the contact surface becomes indistinct. The jelly suitable for alcoholic systems is prepared from collodion by the following method :—

(*a*) In the first instance we may directly place pieces of nitrated cotton, *e.g.*, the commercial *celloidin* of *Schering*, into the solution to be analysed, and then look for any penetration after rinsing the cotton and cutting it open. This gel., wlich is supplied in transparent blocks, is said to contain about 30 per cent. of nitrocellulose and no medium except alcohol. As a matter of fact ether is not quite absent, as the smell indicates. By repeated washing with 97 per cent. alcohol the ether may, at any rate, partly be removed; only traces of nitrocellulose will be dissolved by this operation.

Into such blocks Night Blue and Magdala Red will deeply penetrate within a few hours, whilst the HgS-sol. will not enter into the gel. even in the course of days.

b) When alcoholic collodion jelly is prepared for the test-tube experiment in the usual way, the following difficulties will arise : Even solutions of collodion rich in alcohol do not gelate on cooling, nor in the course of time. The gelation takes place only with change in the concentration, and in the composition of the disperse phase. There is the further difficulty of obtaining the jellies free of ether. The following procedure has answered best : The collodion wool is disintegrated and kept standing for four or five hours with ether until it has completely dissolved. The solution is rubbed with four times its volume of alcohol and evaporated to a thick consistency at 50° or 60° C. Alcohol is again added as before, and the evaporation repeated, several times if necessary. The final solution will be a slightly turbid thickish liquid of about three times the volume of the original solution in ether (containing, therefore, 5 or 6 per cent. of nitrocellulose) faintly smelling of ether. The criterion for the "maturity" of the solution is a strong tendency to surface-skin formation. The solution is poured into test tubes and allowed to stand for 24 hours at ordinary temperature. The skin first forming will gradually thicken, but the solution underneath it may remain fluid for a long time. The formation of a skin thus imparts to the experiment the character of a dialysis, which spontaneously passes into that of a jelly-diffusion. Since the last traces of ether are retained with great persistency, the solutions to be examined should not be sensitive to ether ; that is so in the case of the HgS-alcosol, as was stated above. For the demonstration of these diffusion experiments this HgS-sol and night blue in alcoholic solution may again be utilised.

5. *Some Results of Dialysis and Diffusion Experiments with Solutions in 97 per cent. Alcohol.*—It should be pointed out in the first instance that the HgS-alcosol described could neither be dialysed, nor be diffused with any of the arrangements mentioned, although it passed readily through the densest paper filters of Schleicher and Schüll, 602 e.h. The membranes and gels described were hence, without doubt, impervious to colloids. That could not be ascribed to coagulation at the membrane, although such coagulation was occasionally noticed. It was observed, on the contrary, that the sols, kept merely covered up in the collodion dialyser, or over the diffusion jelly, remained deep dark-brown for 10 days. When poured off finally the sols passed through a baryta filter without any decomposition. On the other

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hand, we frequently found dialysers which were not impervious, and through which the colloid passed in a short time, yet *likewise undecomposed*. The point in question is hence actually the mechanical density of the membrane or gel, and not perhaps any chemical or colloidochemical reaction with the sol.

The dispersoid analysis of substances which are spontaneously soluble in alcohol of 97 per cent. yielded a somewhat surprising result. *So far we have not succeeded in finding any substance, spontaneously soluble in alcohol of 97 per cent., which would not dialyse and diffuse to a perceptible degree.* All the solutions so far studied are, *at least partly*, molecularly-disperse. It is presumable that, in 97 per cent. alcohol, *dispersoids of variable concentration*[4] will frequently occur, *i.e.*, systems, the degree of dispersion of which strongly varies with the concentration, decreasing as the concentration decreases. Only in more concentrated solutions the individuals unite to coarser aggregates. We meet with similar relations in dyes, *e.g.*; at the same time these structures are also " polydisperse "; they contain both molecular aggregates and coarser aggregates, presumably in a definite equilibrium ratio.

Not all the substances enumerated below have been submitted to all the dialyser tests mentioned, although the more interesting substances were analysed by all the methods mentioned. The majority of the tests was made with the collodion and gelatin dialysers and with the collodion jellies. It should, however, be emphasised that membranes of various types gave throughout *equal* results. Substances which passed through gelatin, hardened with alcohol, passed also through collodion or rubber, &c. It should be stated also that the imperviousness of the dialyser to the HgS-sol was in most cases retested after the experiment. Whenever permeability was noticed, the experiment was repeated.

The following substances did dialyse and diffuse :—

Dyes.—Night blue, Magdala red, alkannin, cyanin, alizarine, nigrosin (faintly violet); further six different technical spirit lacquers, &c.

Iodine diffused at a strikingly rapid rate in 97 per cent. alcohol.

Of *resins* dialysed in 97 per cent. alcohol : colophony, copal, mastic, dammar, Burgundy resin, guajac, dragon's blood, &c.

The permeability test is easily made in these cases by dropping the external liquid into a beaker containing water or solution of aluminium sulphate; after dialysing for 24 hours a milky turbidity was always noticed.

Dialysis was further observed with alcoholic solutions of linseed oil, bees' wax, neutral fats (like cocoa fat), lard, &c.; further capric acid, aluminium oleate. The test is here made as first indicated with the aid of water or of a solution of aluminium sulphate. Confusion with traces of collodion, which might be dissolved by the alcohol as stated above, is easily avoided; the collodion is precipitated in films or scales, but does not give rise to a milky turbidity. It is of special interest to mention that an alcoholic albumenoid, zein, is also distinctly dialysed. This material is prepared by extracting granulated maize with alcohol of 97 per cent at 50° or 60° C., and by filtering the yellowish solution. The analytical test was, in this case, performed with the aid of the Essbach reagent (picric acid plus citric acid) after dilution with water to three or four times the volume, or with the xanthoprotein-reaction. Mere pouring into water was

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not decisive since the solution might contain lipoids. Pouring of the external liquid into ether also furnishes a sensitive test. Zein diffuses, in solution in alcohol of 97 per cent., through all the following membranes: parchment paper, collodion, rubber, gelatine. In this case as well the dialysers were subsequently submitted to a test with the HgS-sol. The diffusion experiment into collodion jelly did not lead to any definite result, because zein, differing from the HgS-sol in this respect, is easily precipitated by small proportions of ether.

This dialysis of zein in 97 per cent. alcohol is of special interest because it points undoubtedly to a molecularly-dispersed condition of this albumenoid in that dispersing medium. It would be very desirable to study these solutions from the standpoint of physical chemistry with respect to true solutions, *e.g.*, by determining the boiling point at reduced pressure. So far colloid-chemists have mainly been endeavouring to transform "crystalloids" in the sense of Graham into the colloidal state. The case of zein may indicate the way conversely of transforming Graham's colloids or, more generally, substances of complex chemical composition by gentle methods into the molecularly dispersed state.

Summary

The author describes the preparation of membranes and jellies suitable for the dispersoid analysis of solutions in alcohol of 97 per cent., for both dialysis and diffusion experiments.

The mercury sulphide alcosol, the preparation of which is explained, proves to be an especially stable sol suitable for these tests.

It results that the solutions so far examined, of dyes, resins, neutral salts, fatty acids, soaps, &c., produced by the spontaneous solution of these substances in alcohol of 97 per cent., are all molecularly-dispersed or contain, at any rate, molecularly-dispersed particles in considerable proportions. Zein, the albumenoid of maize which is soluble in alcohol, is also found to be dialysable.

[1] De Mosenthal, *Journ. Chem. Soc.*, **30.** p. 782 (1911).

[2] J. Duclaux and E. Wollman, *Compt. Rend.*, **152.** p. 1580; *Bull. Soc. Chim.*, [4], **27.** p. 414 (1920); "*Le Caoutchouc et la Guttapercha*," p. 10579 (1920).

[3] *Cp.* "*Kleines Praktikum der Kolloidchemie*," Dresden, 1920, Th. Steinkopff, p. 22.

[1] Wo. Ostwald, "*Grundriss der Kolloidchemie*," 6th edition, p. 39 (1921).

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DISCUSSION

Mr. A. Highfield : It has been suggested by Mr. Sproxton that the solvent power of ether-alcohol mixtures of nitrocellulose is due, as was originally proposed by Baker (*J.C.S.*, 1912, T. 1409), to a loosely-held ether-alcohol compound, this complex exerting a solvent power while ether and alcohol do not do so.

The recently published work of Gibson and McCall, if applied quantitatively to this suggestion, seems to render it very improbable. In the first instance, Baker's theory was based merely on certain departures on the experimental values of the viscosity of ether-alcohol mixtures from the calculated values, and can only be said to be but indicative of this ether-alcohol complex.

As regards these ether-alcohol nitrocellulose solutions, given the same concentration, the viscosity of a solution is not necessarily a criteria of the optimum solvent. In the case of solutions, the term "best solvent" implies, of course, greatest solvent power and, incidentally, a clear demarcation of the phases when saturation is reached. In these instances we do not, in general, get this latter phenomena, and it becomes, in consequence, exceedingly difficult to use the ordinary phraseology of solutions. The real meaning of this complex theory is, I take it, that the solvent power of ether-alcohol mixtures is due to this ether-alcohol complex, and that the ether-alcohol mixture which contains the greatest amount of this complex will be the best solvent and will also give the solution with the minimum viscosity. Qualitatively, this is satisfactory enough.

A more quantitative investigation, however, reveals several anomalies. It has been found that nitrocellulose solutions in ether-alcohol containing 2 per cent. of water have a comparatively constant viscosity when considered with those containing 7 per cent. of water, the ether-content being kept within the limits of 10 to 60 per cent. The variations of the former solutions are about 20 per cent. and the latter about 300 per cent. It is clear that the variation in the amount of the ether-alcohol complex is not a predominating factor.

Another consideration is the nitrogen content of the nitrocellulose. Reference to Gibson and McCall's work shows that for 4 per cent. solutions of nitrocellulose and nitrogen content 11·8, the solvent which gives the solution with minimum viscosity contains about 50 per cent. ether and 50 per cent. alcohol. The corresponding solvent for a nitrocellulose containing 12·5 per cent. of nitrogen is about 70 per cent. ether and 30 per cent. alcohol. The explanation of this on this "complex theory" is that the affinity of the former nitrocellulose (11·8 per cent.) for alcohol is greater than the latter. Consequently, in the former instance more alcohol will be required to saturate the nitrocellulose and to give the maximum amount of ether-alcohol compound than in the latter case (12·5 per cent.). This implies that a change of 0·7 per cent. in the nitrogen content of a nitro-cotton involves 20 per cent. of the alcohol in a 4 per cent. solution. It would thus seem that for more concentrated solutions very little alcohol would be available for the formation of the ether-alcohol complex, and that it would be difficult to make these solutions. This is not in accordance with experience.

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Also, if the postulate that the affinity of nitrocellulose for alcohol determines the composition of the solvent mixture which gives the solution a minimum viscosity, a variation of concentration of nitrocellulose, in that it would alter the quantity of alcohol required to "saturate" the nitrocellulose in the system, should result in an alteration of the amount of alcohol necessary for the solution with a minimum viscosity. But it was shown that the solvent required to give this solution was independent of the concentration. Since it is necessary to introduce this property of nitrocellulose (*i.e.*, the alcohol affinity), it is difficult to see how the "complex theory" can explain this experimentally established fact.

Still another objection can be raised on the matter of influence of water. One would expect that mixtures of dry ether and dry alcohol should contain more of this ether-alcohol complex than if water were present in addition. Dry ether-alcohol mixtures should therefore give nitrocellulose solutions of lower viscosity than mixtures containing water. This is not realised in practice. On the contrary, the former solutions are stiff jellies, while under corresponding conditions the latter are fluids. We thus see that, in the light of this somewhat quantitative investigation, this theory appears to be very improbable.

Dr. Irvine Masson: The first effect of "solvents" on nitrocellulose is that they are taken up in some manner and are dissolved uniformly in the substance of the nitrocellulose; and we have to remember that whether a liquid is a so-called gelatinizing solvent or not, depends on one thing that has not been mentioned, and that is temperature. If you take nitrocellulose and moisten it with alcohol, nothing happens; but if you cool this mixture with solid CO_2 at a temperature of 80°, the alcohol is quickly absorbed by and gelatinizes the fibres. With ether containing no alcohol, under similar conditions, you do not get any gelatinization at temperatures attainable with liquid air. Such effects as these, and incidentally the fact that aqueous alcohol at low temperature is a still better gelatinizer than is absolute alcohol, must be borne in mind in considering any general theory of gelatinization.

In connection with the existence of an optimum mixture of binary liquids which gives the minimum viscosity when nitrocellulose is dispersed in it, in the case of ether-alcohol the optimum percentage is somewhere in the neighbourhood of 50 molecules of alcohol and 50 molecules of ether on the average. This would naturally suggest that an equimolecular complex of ether and alcohol is the chief agent in gelatinizing and dispersing; but, while this may be true, there are one or two points which must be borne in mind in making such an inference. We are at a loss to know what is the real composition of the liquid after the nitrocellulose has dispersed itself in it. We do not know how much solvent as a whole has been absorbed by the nitrocellulose to form the gel which has been dispersed, nor do we know the ratio of ether to alcohol in the gel particles. There is undoubtedly a selective absorption by the nitrocellulose, which leaves the composition of the residual fluid at equilibrium different from the original synthetic composition of the solvent. For that reason we must be careful in making deductions from experimental data in which we find a minimum viscosity with a particular *initial* percentage of ether in the alcohol, the percentage being taken before admixture with the nitrocellulose. It is rather difficult to arrive at

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an idea of the amount of liquid which can be so taken up by the nitrocellulose, but one can get an approximation to it by putting nitrocellulose fibrous pulp in vessels kept saturated with the vapour of different mixtures of the two liquids in question. If one does that with these mixtures, it is found that there is a particular mixture from whose vapour the nitrocellulose absorbs far more total weight of material than at any other. There is an optimum mixture, in fact, at which absorption is at its greatest value. It may be nothing more than a coincidence, but it is a fact that that optimum composition is very near to the 50 : 50 molecular ratio which we meet with in studying ether-alcohol viscosity systems. In the matter of complex formation, I think we may defer for the moment to the physicists, who argue on thermodynamic grounds and have shown, as Prof. Porter has shown recently, that from the vapour pressure curves of binary liquids one may not with security deduce the existence of chemical compounds. One may deduce what may be called a mutual interaction between the two liquids concerned, and if we rest content with that, I think that is as far as we are entitled to go for the present. There is undoubtedly some interaction in the particular case of ether and alcohol, and without doubt that interaction favours the absorption of these liquids by nitrocellulose and, as a consequence, the degree to which the nitrocellulose is dispersed; the viscosity and all other physical properties are correspondingly affected.

Mr. F. Sproxton said that the views expressed by Sir R. Robertson on the relation between viscosity and toughness were the opposite of those held in the celluloid industry. The divergence of opinion might be due to the difference in the nitrogen percentage of the nitrocellulose employed, and the presence of camphor in celluloid might affect the question. He thought it more likely, however, that cordite and celluloid received such different handling that a test which would be adequate for one would not be so for the other. Presumably the bending test which Sir R. Robertson described, measured the tensile strength of the outer skin of the cordite. In the celluloid industry little importance was attached to tensile tests. Many celluloid substitutes showed good tensile tests, but little elongation; such materials were brittle and would crack under shock —*e.g.*, if a sheet were brought down sharply on the flat surface of a table. Celluloid made from nitrocellulose of low viscosity was brittle when tested in the same way. The best test of the mechanical value of celluloid was to put a few hundredweights through the shops where articles were made, and note the fraction of material thrown out; but this could not be regarded as a satisfactory position from the scientific point of view.

Mr. F. Sproxton, replying to the discussion, regretted that in his endeavour to be brief, he had apparently given the impresssion that he unreservedly accepted Baker's theory. That was not the case. Baker's deductions were criticised by Bingham, and they were also rendered doubtful by Bramley's work on binary mixtures. Nevertheless, they had not been definitely disproved, and he had attempted to examine recent evidence using the theory as a basis for discussion.

Sir Robert Robertson : I think Mr. Sproxton might have claimed rather more than he did in his paper. He has brought out a matter of great importance in recalling the work of Will on the hygroscopicity

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of nitrocellulose. Will found that the percentage of water taken up by a nitrocellulose together with the nitrogen percentage is a constant, thus showing the extent to which the unesterified hydroxyl groups are capable of taking up water. This seems to me to have a very important bearing on the question of the solubility of nitrocellulose in ether-alcohol solutions. In the first place, when the ether and the alcohol are both anhydrous, nitrocellulose goes into solution only with great difficulty and the viscosity of the solution is very high. Now, when a ternary diagram is constructed from the three constituents of the solution, ether, alcohol and water, we get a minimum viscosity when a considerable amount of water is present, about 8 per cent. with a nitrocellulose of 12·15 per cent. of nitrogen. Dr. Masson and others have found also that acetone in an anhydrous condition is a poor solvent for nitrocellulose, but that when 6 or 7 per cent. of water is present a minimum viscosity is obtained. Again, to-night Dr. Barr has shown us that with acetyl cellulose an acetone and water solution gives a definite minimum of viscosity, acetone-alcohol a much less definite one, and with acetone-benzene a straight line is obtained. It must also be borne in mind that the minimum viscosity of solutions of nitrocellulose, as described in the papers mentioned, was arrived at with ether-alcohol of which the alcohol had 8 per cent. of water. The subject wants following up something on the lines of McCall and Highfield, by working out further ternary diagrams with nitrocelluloses containing different contents of nitrogen. We may then get further information by considering these in conjunction with Mr. Sproxton's suggestion of the possible influence of the unesterified hydroxyl groups in the nitrocellulose. We may thus get nearer to explaining the mysterious question as to why nitrocellulose is dissolved by ether-alcohol, neither of which, by itself, will dissolve it.

The cords of nitrocellulose of high nitration were manufactured so as to be all of the same diameter, thus avoiding corrections on the application of the test for fragility on bending. When nitrocelluloses of different degrees of nitration are tested for viscosity in acetone, it is found that a striking fall in viscosity sets in about the region at which they would become soluble in ether-alcohol. Below this are the usual soluble nitrocelluloses, but the nitrocellulose used for the experiments described has a high degree of nitration and a very high viscosity. Attention was called to the effect produced as an example of the need for following up the investigation of the physical properties of solutions of increasing concentration right up to the solid product from which the solvent has been dried out, a subject which includes work on such substances as celluloid.

Mr. W. Harrison (*communicated*):

With regard to the observation of Duclaux and Wollman referred to in Mr. Sproxton's paper, that nitrocellulose solution can be separated into fractions giving widely different viscosities, it is interesting to note that starch solution can be separated by alcohol in a similar manner. In the case of starch, however, it has been found that the various fractions are apparently interconvertible. The most soluble fraction can be converted into a less soluble form by drying, and the least soluble form rendered more soluble by disintegration such as by the vigorous shaking of the solution.

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Dr. G. Barr and Mr. L. L. Bircumshaw (*communicated*) :

The minima in the viscosity concentration curves for acetone water and acetone-alcohol are, perhaps, most simply explained on the assumption that the " best solvent " for cellulose acetate is the unimolecular form of acetone, and that the degree of dispersion is reduced by the presence of either associated acetone or of the diluent added. Acetone is usually supposed, mainly on the evidence of the variation of surface-tension with temperature, to consist largely of a trimolecular form. The addition to it of the strongly associated substances, water or alcohol, would rapidly increase the concentration of unimolecular acetone, water being more effective than alcohol, and so increase the solubility of the cellulose acetate : this solubility would eventually be reduced, and the viscosity increased, by the further addition of water or alcohol since the acetate is comparatively insoluble in these liquids. Benzene, being practically non-associated, would be less efficacious in increasing the proportion of unimolecular acetone, and since it has even less solvent action than alcohol, the absence of any fall in viscosity is readily understood on this view.

A study of the physical properties of binary mixtures of acetone with the three diluents used in the above investigation has revealed no evidence which would point to the production of a complexes such as that postulated by Baker for his ether-alcohol mixtures to explain the solubility of nitrocellulose. The only obvious maximum in the curves connecting density, surface-tension or viscosity with molar concentration, occurs at the water end of the viscosity concentration curve for acetone-water.

A similar hypothesis would appear to afford a simpler explanation of the variation of solubility and of viscosity of the solutions of nitrocellulose in ether-alcohol with the composition of solvent mixture than was suggested by Baker. The " best solvent " for nitrocellulose would, on this view, be non-associated alcohol, the proportion of which would be increased by the admixture of ether. Since ether is very little associated a considerable volume must be added to give a large proportion of unimolecular alcohol. The effect of small quantities of water on the solubility in ether-alcohol is qualitatively predicable from the hypothesis. The variation of the composition of the optimum mixture with the hygroscopicity of the nitrocellulose to which Mr. Sproxton has referred, and of which he mentions an explanation based on the ether-alcohol-complex theory, is capable of a somewhat similar interpretation on the hypothesis that non-associated alcohol is the most active dispersion medium.

The suggestion which we have advanced in the hope of stimulating discussion and research on these interesting relationships has, it would appear to us, the following advantages over a theory involving the assumption of the formation of a complex :—

(1) It is in accord with the known effects of the dilution of an associated liquid by another of any degree of association, and does not require the postulation of a compound for the existence of which there is little or no evidence.

(2) The assumption that simple molecules possessing considerable " residual affinity," are more readily attached to the cellulose ester molecule, *i.e.*, are better solvents than are the associated forms seems more probable than the ascription of similar facility of attachment to a more saturated complex.

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(3) It avoids the necessity of assuming the existence of a fresh complex for each diluent considered: the same hypothesis explains the increased solubility of nitrocellulose in mixtures of alcohol either with ether or with toluene, and of acetylcellulose in mixtures of acetone either with water or alcohol.

(4) The very large influence of temperature on the dispersion (as indicated by viscosity) of colloidal solutions such as these, is obvious on the theory which we propose, since rise in temperature rapidly increases the proportion of unimolecular solvent; on the complex theory the proportion of complex would have to decrease with rise in temperature unless it were endothermic.

Dr. H. P. Stevens: Mr. Porrit has described the changes taking place in rubber under two heads: the first in which the rubber becomes tacky, and the second in which it becomes brittle. I do not think a rubber necessarily goes through both these changes. I think he will agree with me that a raw rubber becomes tacky, whereas a vulcanized rubber becomes brittle. When vulcanized rubber goes brittle with age, the change is apparent owing to a gradual stiffening, and the rubber does not pass through any tacky stage. I think the author's discovery of the gel formation of a raw rubber sol in a sealed tube is a new and exceedingly interesting one.

(*Communicated*):

Mr. Porrit states in his paper: "It is surprising that none of the published investigations dealing with the perishing of rubber contain any reference to the pungent acid odour which under ordinary conditions is a well-marked feature of the change" (perishing of rubber).

Mr. Porritt did not read his paper *in extenso* at the meeting and a printed proof was not available, otherwise I should have remarked on the above paragraph. I was, I believe, the first to examine the pungent acid odour to which Mr. Porritt refers, and the matter is dealt with in my paper on the "Nature of Vulcanisation" (*Jour. Soc. Chem. Ind.*, July, 1919, p. 196T). where I wrote as follows: "During ageing, vulcanised rubber emits a pungent odour and gives off acid vapours due to a trace of a volatile product containing sulphur. When passed into water, this substance is retained and the solution reduces ammoniacal silver nitrate."

As the perishing of rubber is a process of oxidation, it is curious that the vapour given off should have reducing properties.

Dr. E. H. Rayner: With regard to the effect of light on rubber, I should like to emphasize the importance of the effect of light on ebonite, which is a very serious matter. For many years we have been very much troubled with it. Ten years ago, at the National Physical Laboratory, we did a long research on all kinds of ebonite. One of the objects was to find an ebonite, if possible, that was not affected by light. Of 20 or 30 samples we obtained, we did not find a single one that did not act as a sulphuric acid manufacturing plant when exposed to daylight, especially in a damp atmosphere. These 30 samples have now been exposed to light for 10 years, and they still go on generating sulphuric acid. They get washed occasionally with alkali and soap, but they start again, and this morning I tried one by putting a penny on a piece of ebonite and connected it to a low-resistance portable galvanometer. A pen-knife was connected with the other terminal of the galvanometer, and quite an appreciable

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deflection was produced. The insulation resistance was of the order of 1/20th megohm with two pennies half-an-inch apart. That being so, the leakage across the ebonite mounting of a standard resistance of the order of a megohm may be important with ebonite in a very much better condition than the sample mentioned. We have had to design resistances to avoid this trouble, but the production of an ebonite which is not affected by light is badly wanted in the electrical industry, especially where the laboratories have a top light and a damp atmosphere. If, therefore, somebody can suggest a method of making ebonite which is not so affected, we should be very grateful.

Prof. A. W. Porter : Even sulphur itself becomes conducting under the action of light, and perhaps the conducting power in ebonite is one that is simply inevitably associated with it, and you will never be able to get rid of it without getting rid of the sulphur. Sulphur behaves something like selenium, only to a smaller extent.

Mr. Rayner : Does sulphur form sulphuric acid in the air ?

Prof. Porter : I do not know what change occurs, but it becomes conducting.

Dr. Stevens : The moisture no doubt helps conductivity. The sulphuric acid is formed and absorbs moisture. You cannot have anything better than a damp atmosphere to prevent oxidation taking place.

Mr. B. D. Porritt : The serious deterioration in the insulating properties of ebonite resulting from exposure to light, to which Dr. Rayner has made reference, is almost certainly due to the formation of a film of sulphuric acid on the surface. This probably is to be attributed to the oxidation of free sulphur since the rubber sulphur compound which constitutes ebonite is a relatively stable compound.

In respect to Dr. Stevens's remarks on the subject of " tackiness," this is certainly a characteristic of raw rubber and is not manifest during the changes which take place during the oxidation of vulcanised material regarding which comparatively little is known.

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SECTION V.—PRECIPITATION OF DISPERSE SYSTEMS

A communication by **Dr. R. S. Willows** opened the consideration of this section of the subject.

THEORY OF PRECIPITATION OF DISPERSE SYSTEMS

BY

R. S. WILLOWS, M.A., D.Sc., F.Inst.P.

The subject of colloids has hitherto attracted few English workers in physics in spite of the splendid field for research. One object of the discussion is educative: to show the extent and interest of this field. It was this aspect that was mainly kept in view in the preparation of this note.

Of nearly all the work on precipitation of sols or emulsions by added electrolyte the common criticism can be made that faulty methods are used for determining when the same definite stage in the precipitation has been reached. Thus the settlement of the precipitate in an arbitrarily chosen time or a fractional change in viscosity have been used to fix a measuring point, but their connection with the earliest stage of precipitation—the coalescence of pairs of colloid particles—is at best a distant one and is perhaps masked by other factors. Some work by Zsigmondy and his pupils on rapid coagulation appears to be quite definite in its results and has the further advantage for our present purpose, that the conditions chosen are such as to admit of its mathematical treatment.

Zsigmondy finds it is possible in the ultra-microscope to distinguish between the yellow-green primary and the secondary particles in a gold sol, the latter being formed by the coalescence of two primary particles. The method of experiment is as follows:—Having determined, by counts in an ultra-microscope, the number, N, of primary particles per unit volume of a red gold sol, electrolyte is added in a definite volume: when a certain easily recognised colour tint appears a solution of gum arabic is added, which by its protective action stops further coalescence. A recount is now made either of (*a*) the primary particles per unit volume, N_1 in number (Zsigmondy), or (*b*) the total number, ΣN, of particles, primary, secondary, &c. (Westgren and Reitstötter). These can be compared with the results calculated from Smoluchowski's theory, of which an outline is given below.

Earlier experiments on precipitation have shown a marked influence of the nature of the electrolyte, when the time of coagulation is an hour or longer, but these of Zsigmondy's, on rapid coagulation, show that for the gold sol used the time of coagulation cannot be reduced below five or six seconds with electrolyte concentration varying between fairly wide limits, and that this time is independent of the valency, &c., of the ions. Rapid coagulation is, in fact, conditioned entirely by rapidity of diffusion. By comparing the results obtained, when different amounts of electrolyte are added, with others of Galecki, in which he relative charges on the sol particles are measured, the conclusion

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is reached that rapid coagulation occurs before the iso-electric point is reached. This agrees with Powis's results on emulsions; but whereas Powis found that it was sufficient to reduce the potential difference across the double layer from 0·04 to 0·03 volts in order to start coagulation, the discharge of the gold particles had to be much more complete.

In his theory of these experiments Smoluchowski assumes that the particles attract each other by "capillary" forces (nature not specified) when they approach each other, but that normally coalescence is prevented by the double electric layer which must first be broken. When electrolytes are added this layer is wholly or partially destroyed by ionic adsorption (mechanism not specified). Brownian motion tends to bring the particles into contact, and he further assumes that whenever the distance between two centres becomes less than R′ that coalescence occurs.

By a beautiful piece of mathematical work the author calculates the number of primary particles N_1, the secondary particles N_2, &c., and the total number of particles of all classes, ΣN, present in unit volume at a time t after the addition of electrolyte. To save space, only Zsigmondy's results are dealt with here. The equation from which to calculate N is :—

$$4\pi DRN = \frac{1}{t}\left[\sqrt{\frac{N}{N_1}} - 1.\right].$$

where Einstein's diffusion constant $D = \frac{R\theta}{n} \cdot \frac{1}{6\pi\mu r}$

R = gas constant.
n = Avogadro's number.
μ = viscosity of medium at abs. temp. θ.
r = radius of particles.

Some of the results are given in the table.

t(secs)	N_1 obs.	N_1 calc.
2	1·42	1·71
10	1·17	1·14
20	·75	·76
30	·52	·53

It should be noticed that Smoluchowski's work is entirely statistical; he does not attempt to account either for the double layer, the adsorption of the electrolytic ions or for the assumed attraction between the sol particles. A complete theory must explain the origin of the charge on the particles and how the discharging ions penetrate the double layer against the repulsion of the external half.

Two points appear to be fairly established. The stability, at least of emulsions, depends only on the potential difference across the double layer, as shown by Powis; and, contrary to Bredig's theory, Ellis finds no relation between surface tension and the coagulation of emulsions.

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THE ORIGIN OF THE CHARGE OF A COLLOIDAL PARTICLE AND ITS NEUTRALISATION BY ELECTROLYTES

BY

JNANENDRA NATH MUKHERJEE

The origin of the charge of a colloidal particle is generally referred to the adsorption of ions. Regarding the mechanism of the adsorption we have no definite idea. In his theory of adsorption Langmuir* refers it to "chemical forces" due to the surface atoms. The adsorption of an ion gives a charge to the surface, and as a result introduces electrical forces. The recognition of this factor elucidates the influence of electrolytes on the precipitation of suspensoids on electro-endosmosis and allied phenomena.

The Charge of Suspensoids

It is well known that the stability and the charge of suspensoids are connected with traces of electrolytes. Table 1 shows that for most suspensoids *the charge is of the same sign* as that of the "ion" the substance has in common with the peptising or stabilising electrolyte. Most suspensoids (excepting colloidal metals and other elements) are included in the table.

Table 1

Suspensoid.	Stabilising Electrolyte.	Common Ion.	Sign of the Charge of the Particles.
[1] Insoluble silver salts	(*a*) Silver nitrate	Ag°	Positive.
	(*b*) Electrolyte with common anion.	Anion	Negative.
[2] Metal sulphides	Hydrogen sulphide or ammonium sulphide.	S'' or HS'	Negative.
[3] Ferrocyanides of copper, and iron.	Potassium ferrocyanide	Anion	Negative
[4] Hydroxides of iron, aluminium, etc.	Nitrate or chloride of the corresponding metal.	Cation	Positive.
[5] Hydroxide of iron	Alkali hydroxide	Hydroxidion	Negative.
[6] Barium carbonate	Barium nitrate	Barion	Positive.

References

[1] Lottermoser, *Koll. Zeitsch.*, 1910, **6**, 78 (*see also* earlier papers).

[2] Linder and Picton, T., 1892, **61**, 114; T., 1905, **87**, 1914; Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; Young and Goddard, *J. Phys. Chem.*, 1917, 21, 1; Mukherjee and Sen, T., 1919, **115**, 461.

[3] Duclaux, *Compt. Rend.*, 1904, **138**, 144, 571; *J. Chim. Phys.*, 1909, (vii), 405.

[4] Pauli and Matula, *Koll. Zeitsch.* 1917, **21**, 49; Duclaux, *J. Chim. Phys.*, 1907, **5**, 29.

[5] Powis, T., 1915, **107**, 818.

[6] Perrin, *J. Chim. Phys.*, **2**, 1904, 601.

Compare also for "stannic hydroxide" Biltz, *Ber.*, 1904, **37**, 1095 and Glixelli, *Koll. Zeitsch.*, 1913, **13**, 194.

The relationship shown in Table 1 makes it possible to define the chemical forces involved in this particular case. The fixation of a common ion is due to the same causes that bring about the growth of a crystal in its solution.

* *J. Amer. Chem. Soc.*, 1916, **38**, 2221; *ibid.*, 1917, **39**, 1848.

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The growth of a crystal in its solution shows that the surface atoms of a solid attract the molecules of which it is composed, and that the " atoms " or " groups " in the molecule are attracted most strongly at specific points in the surface. The " attached " molecule thus conforms to the structure of the crystal. As an example one may say that at the surface of a crystal of sodium chloride there are " places " where the chlorine ion in salt solution can be held by chemical forces. The specific nature of chemical forces requires that the same attraction will be present when the crystal is in contact with any other solution of an electrolyte, which gives a " chlorine ion " in an aqueous solution. Thus on the addition of hydrochloric acid the chloridions will be attracted. If " N " be the number of " places " per unit surface where the chloridions are attracted chemically, then the number remaining " attached " to the surface (at any instant) will be dependent :—

(1) On the concentration of the " ion," and

(2) " A " the work necessary to separate the " ion " from its position in the surface. " A " is evidently the measure of the chemical affinity acting on the " ion," and $e^{-A/kT}$ is a measure of the stability of the " fixation " where $k = \frac{R}{N_o}$, R being the gas constant, No the Avogadro number, and " T " is the absolute temperature. For a stable union it is necessary that " A " should be great compared to kT. In this case a small amount of an electrolyte with an adsorbable " ion " will be sufficient to lead to the adsorption of an appreciable amount of the " ion." Since the molecules of sodium chloride and hydrochloric acid do not combine with each other in their entirety this sort of " fixation " of the chloridion will impart a charge to the surface.

The resulting separation of electricity will be opposed by the electrical attraction exerted by the cations in the surrounding liquid.

The Electrical Attraction on Ions of Opposite Charge

We shall speak of the " ions " fixed to the surface by chemical forces as " chemically adsorbed." *In the following discussions it is assumed that there is no chemical affinity acting between " ions " of opposite charge.* This assumption is obviously made to investigate the effect of the electric forces alone.

In consequence of the charge, ions of opposite sign will be drawn near the surface. In the liquid there remains an equivalent amount of ions of opposite sign. The electrical energy will be minimum when these ions are held near the surface so that the distance between the oppositely charged ions has the nimumum value possible under the conditions, and they will be held opposite to the ions chemically adsorbed. An " ion " so held will not be " free " to move if its kinetic energy is less than " W ", the energy required to separate the ion from the oppositely charged surface.

The number of such " bound " ions determine the diminution in the charge of the surface. When the concentration of ions of opposite charge in the liquid is small the number of ions " held " to the surface by electrical attraction will be small. The equilibrium conditions will be discussed more fully later.

If the chemically adsorbed ions have a valency equal to " n_1 " and " n_2 " is the valency of the oppositely charged ions in the liquid in contact with the surface then

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$$W = \frac{n_1 n_2 E^2}{D x} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where E = the electronic charge, x = the distance between the centres of the " ions " at the position of minimum distance, and " D " is the dielectric constant of water. Since " ions " have probably an envelope of water " x " has a value of the order of 10^{-7} *cm* (the diameter of the molecules of water is about 4×10^{-8} *cm.*). The probability of an ion remaining fixed is given by $1 - e^{-W/kT}$ where " k " and " T " have the same significance as before. The values of $1 - e^{-W/kT}$ for different values of n_1 and n_2 are given below.

TABLE 2.

$x = 10^{-7} cm$. D = 81. Values of $1 - e^{-W/kT}$

T = 27°C · $k = 1{\cdot}37 \times 10^{-16}$
E = $4{\cdot}77 \times 10^{-10}$ C.G. S units.

	$n_2 = 1$	$n_2 = 2$	$n_2 = 3$	$n_2 = 4$
$n_1 = 1$	·501	·751	·875	·938
$n_1 = 2$	·751	·938	·984	·986
$n_1 = 3$	·875	·984	·998	X

Since the value of " x " is not known definitely, Table 2 conveys a rough idea of the order of magnitude of $1 - e^{-W/kT}$

A consideration of the values given above will show that the electrical attraction is sufficiently strong to account for the adsorption.

THE DOUBLE LAYER

Depending on the concentration of the oppositely charged ions in the liquid near the surface at any instant a certain number of the " chemically adsorbed " ions are " covered " by " ions " of opposite charge. In the liquid near the surface there are always a number of free " ions " equivalent in amount to the " uncovered " chemically adsorbed ions on the surface. The total amount of ions of opposite sign both " bound " and " free " is equivalent to the amount of ions " chemically adsorbed." These " free " ions form the second sheet of the double layer. It is evident that as a result of their thermal motion the mean distance between the two layers will be greater than " x."

CONDITIONS WHEN EQUATION 1 HOLDS GOOD

" W " has the value given in Equation 1 when the mean distance between the chemically adsorbed ions is considerably great compared to " x," *i.e.*, molecular dimensions. The two oppositely charged ions can then be assumed to be uninfluenced by neighbouring ions on the surface. The considerations set forth below show that for practical purposes we can treat the charge of the surface as due to discrete charged particles widely separated from each other compared to molecular dimensions.

Following Helmholtz and Lamb (*Brit. Assoc. Rep.*, 1887, p. 495; *Phil. Mag.*, 1888, p. 60) it is usual to consider the thickness of the double layer to be of the order of molecular diameters. McTaggart (*Phil. Mag.*, 1914, [6], **27**, 297) calculates the " density " of the charge at the surface of gas bubbles to be $1{\cdot}5 \times 10^4$ C.G.S. units (from the well-known Lamb-Helmholtz equations). He assumes that a layer of water of thickness of about 10^{-8} cm. separates the opposite charges. Since the electronic charge is $4{\cdot}77 \times 10^{-10}$ C.G.S. units (Millikan's value) the number of univalent " ions " which must be adsorbed per unit surface (cm^2) is equal to about 10^{13}. The mean distance between the " ions " will be about 3×10^{-6} cm. The

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distance is greater if the charge is due to adsorbed polyvalent "ions." For a thickness of the double layer of the order of 10^{-6} cm. the mean distance is 3×10^{-5} cms. Similar values of the "density" of the charge are obtained from other data (cp. Lewis, *System of Physical Chemistry*, 1916, Vol. 1, p. 407). Thus we find that the "ions" imparting the charge to the surface are situated wide apart compared to molecular dimensions. Under these conditions the neighbouring ions have comparatively little effect on an oppositely charged "ion" at its position of minimum electrical energy and "W" as given in Equation 1 can for practical purposes be taken to be the measure of the stability of the electrical adsorption of ions of opposite charge.

The Maximum Electrical Adsorption on the Addition of an Electrolyte

It will appear from Table 3 that the addition of an electrolyte with univalent "ions" of opposite sign to the charged surface seldom produces a reversal in the original charge. If, however, the electrolyte has a bivalent ion of opposite sign reversals are sometimes observed. On the other hand, with electrolytes having multivalent ions of opposite sign a reversal of the charge is more frequent.

Table 3

Substance.	Sign of Charge.	Electrolytes.	
		No Reversal.	Reversal.
[1] $CrCl_2$	Made "positive" by the addition of acid.	$Ca(NO_3)_2$, $MgCl_2$	$K_3Fe(CN)_6$. $K_4Fe(CN)_6$
[2] $CrCl_3$	Made negative by the addition of alkali.	$MgCl_2$, $MgSO_4$	$Ba(NO_3)_2$, $Ca(NO_3)_2$
[3] Al_2O_3	"Positive" with acid.	$Ca(NO_3)_2$	$K_4Fe(CN)_6$.
[4] Al_2O_3	"Negative" with	x	$Ca(NO_3)_2$.
[5] Mn_2O_3	"Negative" with base.	x	$Ba(NO_3)_2$.
[6] Carborundum.	"Negative" with base.	x	$La(NO_3)_3$.
[7] Glass	Negative	K_2SO_4, KNO_3, NaCl	Thorium nitrate.
[8] Quartz	Negative	HNO_3, $Ce(NO_3)_3$, $UO_2(NO_3)_2$. $AgNO_3$, $Al_2(SO_4)_3$, $BaCl_2$, $CaCl_2$.	Thorium nitrate.
[9] Copper hydroxide.	Positive	KCl, K_2SO_4, $Al_2(SO_4)_3$	K_3PO_4, $K_3Fe(CN)_6$
[10] Gas bubbles	Negative	HCl, HNO_3	$La(NO_3)_3$, $Th(NO_3)_4$. $Zr(NO_3)_4$, $Al_2(SO_4)_3$.
[11] Silver, gold	Negative	x	$Al_2(SO_4)_3$.
[12] As_2S_3	Negative	KCl, $BaCl_2$, $Al_2(SO_4)_3$	$Th(NO_3)_4$.
[13] Emulsions	Negative	KCl	$BaCl_2$, $Al_2(SO_4)_3$, $Th(NO_3)_4$.
[14] Gas bubbles	"Positive" with thorium nitrate.	x	$K_3Fe(CN)_6$ $K_4Fe(CN)_6$.

References

[1-6] Perrin, *loc. cit.*

[7, 8] Elissafoff, *Zeitsch. Physikal Chem.*, 1912, **79**, 385.

[9, 11] Burton, *Physical Properties of Colloidal Solutions*, 1916, 151, 153.

[10, 14] McTaggart, *Phil. Mag.*, 1914(6), **27**, 297, 12; Powis, T., 1916, **109**, 734.

[13] Powis, *Zeitsch. Physikal. Chem.*, 1914, **89**, 91, 186; also T., 1915, **107**, 818.

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It is difficult to reconcile these facts with the specific nature of the " adsorption " of ions. They are, however, a necessary consequence of the view advanced here. Let us suppose that the " primary ions " which are chemically adsorbed are all univalent. An ion of opposite sign entering the " double layer " will be driven towards the surface by the strong electric field. An " ion " of the same sign will rarely strike the surface. The oppositely charged ions will be held to the surface by electrical forces near each primary ion. The maximum number of ions which can possibly be held in this manner per unit surface is equal to the number of primary ions in the same area. If the oppositely charged ions are univalent it is evident that when the maximum adsorption has been reached the surface is neutral. In general when the primary ions are univalent the maximum possible charge per unit surface is equal to—

$$NE\,(1-n_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where " N " is the number of univalent " primary " ions per unit area, E, the electronic charge and " n " the valency of the oppositely charged ions.

For the general case the possible maximum charge is given as

$$NE\,(n_1 - n_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where " n_1 " is the valency of the " ions " chemically adsorbed and N, E and n_2 have the same significance as before.

Thus a reversal of charge by " electric adsorption " is theoretically possible only when the added electrolyte has an oppositely charged ion with a valency greater than the primary ions. For univalent " ions " of opposite sign reversal is impossible by electrical adsorption. In considering particular cases it should be remembered that " chemical action " is quite possible. It is satisfactory to note that in Table 3 there is not a single case of reversal with univalent ions of opposite sign.

Actually, however, the maximum adsorption will coincide with the neutralisation of the surface. The collisions of " ions " of opposite sign are mostly due to the electrical field of the double layer, and the collisions due to " diffusion " are comparatively negligible. The number of collisions will diminish rapidly with increased electric adsorption, and will have a small value at the neutral point. Farther adsorption will impart to the surface a charge of the same sign as the " ion " and the double layer will now repel the " ion " from the surface. The number of collisions will decrease rapidly and will soon be negligible. Thus a reversal of charge is only possible when the valency of the oppositely charged ion is very great, so that $1-e^{-W/kT}$ has a considerable value. Even then the theoretical maximum adsorption is not possible, and the reversal in charge can proceed only to a small extent. In the majority of cases, therefore, the maximum adsorption will correspond to a neutralisation, or reversal to a slight extent.

Equilibrium Conditions

In discussing the equilibrium conditions we shall deal with the case when the maximum adsorption corresponds to the neutralisation of the charge. The " maximum " amount of an ion of opposite sign that can be adsorbed per unit area is thus equivalent to the charge per unit area. If the charge of the surface is due to " N " ons of valency n_1 per unit area, then the maximum number N of an

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"ion" of valency "n_2" and of opposite signs which can be adsorbed electrically is given by the relation

$$N_m = N.n_1/n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)^*$$

Let "θ_1" denote the fraction of this maximum which has been adsorbed when equilibrium has been reached in presence of ions of opposite sign having a concentration "c" in the liquid. For equilibrium the number of electrically adsorbed ions becoming "free" in any interval per unit area must be equal to the number re-adsorbed in the same time.

Considering unit surface the rate at which the adsorbed ions of opposite charge become "free" is evidently given by

$$k_1.N_m.\theta_1.e^{-W/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since $N_m\theta$ is the number of "ions" adsorbed per unit surface k_1 is a constant.

The rate of adsorption depends on two factors: (*a*) the rate of collision of oppositely charged ions, and (*b*) the number of "places" where adsorption is possible; that is, the number of primary "ions" that remain "uncovered" and unneutralised by oppositely charged ions at any moment. (*Cf.* Langmuir.) This is given by

$$N - N_m\theta_1 = N\left(1 - \frac{n_1}{n_2}\,\theta_1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The rate of collisions (*a*) is determined by the concentration of ions of opposite sign in the liquid in contact with the surface and the forces driving the ions towards the surface. Each "ion" is urged to the surface by two forces:—

(1) *Its thermal agitation to which its osmotic pressure is due.*—According to Einstein this force is equal to $\frac{RT}{No}$.

(2) *The electrical attraction exerted on the particles by the charged surface.*—An ion in the double layer is acted on by its electrical field. The intensity of the field is proportional to the "density" of the charge on the surface, and is, therefore, given by:

$$k'_2(1-\theta_1)n_1N.n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

Since "n_1" and "N" are constants for the same surface we may write (7) as—

$$k_2(1-\theta_1)n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$ where k_2 is a constant.

The thickness of the surface layer is small and the rate of fall in the potential, that is, the intensity of the electric field, is enormous. A simple calculation will show that RT/No is negligible in comparison to $k_2(1-\theta_1)$. Under the conditions the rate of collision is given by—

$$k_3n_2(1-\theta_1).C.u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

where "C" is the concentration of the "ions" in the liquid in contact with the surface, "u" is the "mobility" of the "ion" (under unit force), k_3 is a constant, and "n_2" and "θ_1" have the same significance as before.

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* Equation "4" holds when n_2 is equal to or greater than n_1. When $n_1 > n_2$ more than one "ion" of opposite charge should be adsorbed for each chemically absorbed "ion" to neutralise its charge. The mutual repulsion of these "ions" brings in complications which will not be considered in the present paper.

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From (6) and (8) we find that the rate of adsorption is given by—

$$k_4.N(1-\frac{n_1}{n_2}\theta_1).n_2(1-\theta_1)\ C.u. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

Finally, for equilibrium we get

$$k_1 N_m \theta_1 e^{-W/kT} = k_4 N(1-\frac{n_1}{n_2}\theta_1)n_2(1-\theta_1)\ C.u. \quad . \quad . \quad . \quad (10).$$

Putting $N = \frac{N\ n_1}{n_2}$ and remembering that N_1, n_2, u and $e^{-W/kT}$ are constants for the same ion we can write equation (10) in the form

$$\theta_1 = k_0 \frac{n_2}{n_1}\ C.(1-\frac{n_1}{n_2}\theta_1)(1-\theta_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $k_0 = \frac{k_4}{k_1}\ n_2.u.e^{-W/kT}$.

[It may be stated that k_4 contains the term " $n_1 N$ " (*cf.* equation 7).]

Since " θ_1 " denotes the " fraction " of the original charge neutralised by adsorption the charge of the surface is proportional to

$$1-\theta_1=\theta_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

Equations (1) and (10) show that the " electrical " adsorbability of an " ion " of opposite charge is dependent on its mobility and its valency. Thus for a " negative " surface the order of adsorption of the following cations should be

$$Th > Al > Ba > Sr > Ca > Mg > H > Cs, Rb > K > Na > Li.$$

(Rubidium and Caesium have practically the same ionic mobility.)

It should be remembered that all along we have assumed that the surface does not exert any chemical affinity on the " ions." Clearly this is not likely to be the case always, and the order given above cannot be expected to hold good in such instances. The following section will show, however, that the above order holds good in a large number of cases.

The Precipitation of a Suspensoid by an Electrolyte

It was first pointed out by Hardy that the precipitation of suspensoids by inorganic electrolytes is due to a diminution in the electric charge of the particles. The " ion " having a charge of the same sign on the colloid has very little influence on the precipitation and the precipitating power of an electrolyte is determined by the " valency " of the " ion " which has a charge opposite in sign to that of the colloid. The same results have been observed in experiments on cataphoresis and electro endosmosis (*cp.* the works of Perrin, Burton, Elissafoff, McTaggart, Ellis, Powis, &c.). These regularities are not consistent with the specific nature of the adsorption process as it is ordinarily understood, and they show that the process of " adsorption " in these cases is " electrical " in nature.

Whetham (*Phil. Mag.*, 1899, **48**, 474) recognised the electrical nature of the process, and considering the probabilities of a charged particle meeting an equivalent amount of electrical charge of opposite sign in the form of ions deduced his interesting relation between the precipitating powers of " ions " of different valency.

In the application of his equation of adsorption isotherm to this process Freundlich (*Zeitsch. Physikal. Chem.*, 1910, **73**, 404) assumed that different ions are equally adsorbed at equal concentrations, the constants in the equation being independent of the nature of the " ion."

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Subsequent work has shown that the simple relations indicated by these equations (of Whetham and of Freundlich) do not agree with observations. These theories do not attempt to elucidate the difference in the precipitating powers of "ions" having the same valency. Bancroft (*J. Phys. Chem.*, 1915, **19**, 363; *Rep. Brit. Assoc.*, 1918, Section B., pp. 2–16) and Wo. Ostwald (*Koll. Zeitsch.*, 1920, **26**, 28, 69) have admirably summarised the present position of the subject.

It is necessary to point out in this connection that the precipitation of a suspensoid by electrolytes is a complicated process. The diminution in the electric charge is undoubtedly responsible for the coagulation, but the precipitating concentration of an electrolyte is dependent on such other factors as the distance between the particles, their size, the total amount of colloid-liquid interface and "age." Ions of different valency (and hence different coagulating powers) are not all similarly affected by variations in these conditions. A diluted sol of arsenious sulphide requires a higher concentration of potassium chloride but a lower concentration of barium chloride than what the original sol requires. The ratio of the precipitating concentration of two electrolytes is thus variable (Mukherjee and Sen, T., 1919, **115**, 462; Mukherjee, T., 1920, **117**, 350; Kruyt and Duin, *Koll. Chem. Beihefte*, 1914, **5**, 269; Kruyt and Spek (*Proc. K. Akad. Wetenschap.*, Amsterdam, 1915, **17**, 1158). It is therefore clear that the precipitating concentrations (*i.e.*, the precipitating powers) of an electrolyte cannot be taken as a *quantitative* measure of the adsorption of the "ions." The discussion of such data from a quantitative point of view of adsorption is thus not possible. As a result no direct quantitative relationship is possible between the diminution in the electric charge of a colloidal particle and the coagulating concentration. The precipitating powers of different ions thus give a qualitative measure of their adsorbability.

It will be seen from Table 4 that the order of the precipitating power of cation (on "negative" suspensoids) is as follows:—

Th>Al>Ba>Sr>Ca>Mg>H>Cs,Rb>K>Na>Li

the same as deduced from equation (10).

TABLE 4

Order of Precipitating Power of Cations for various Suspensoid Systems

1. Arsenious sulphide under different conditions.	Th>Al>Ba>Sr>Ca>Mg>H>K>Na>Li.
2. Gold	Al>Sr>Ca>Mg>H>Cs>Rb>K>Na>Li
3. Platinum	Al>Ba>K>Na.
4. Copper ferrocyanide	Al>Ba>H>Cs>Rb>K>Na>Li.
5. Prussian blue	Al>Ba>H>Cs>Rb>K>Na>Li.
6. Silver	Al>Ba>Sr>Ca>H>Cs>Rb>K>Na>Li.
7. "Oil" emulsions	Al>Ba>Sr>Ca>Mg>K>Na>Li.

REFERENCES

Freundlich, *Zeitsch. Physikal Chem.*, 1903, **44**, 129; Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2024; *loc. cit.* Other "sulphides" behave similarly.

Galecki, *Zeitsch. Anorg. Chem.*, 1912, **45**, 221; Westgren, *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 6, 1–30.

Freundlich, *Kapillarchemie*, 1909, 352; 4, 5; Pappada, *Koll. Zeitsch.*, 1910, **6**, 83, 1911, **9**, 136, 6; Pappada, *Gaz. Chim.*, 1912, **42**, I., 263.

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7. The series given refer to both the order of the de-emulsifying power and the effect on the inversion of phase (privately communicated by Mr. S. S. Bhatnagar, *see also* T., 1920, 117, 542. *Also* Bach (*J. Chim. Phys.*, 1920, **16**, 46) finds the series

$$Cs>Rb>NH_4>K>Na>Li$$

for a number of cases).

It should be noted that in the experiments referred to in Table 4 inorganic " ions " only have been used, and that these cations have very little tendency to complex formation. The " alkali " metal cations have the least tendency for complex formation, and it is to be expected that they are most likely to be least affected by chemical affinity due to the surface atoms, and hence the " adsorption " should be mainly " electrical " in nature. The order of alkali cations as deduced from equation (10) determines the order of their precipitating powers in most cases. Pappada* first pointed out that the order of coagulating power of these ions is the same as the order of the mobility.

The Effect of Electrolytes on Electro-Endosmosis

A verification of equation (10) is possible from the experimental work on electro-endosmosis. Unfortunately the experimental difficulties are considerable and the limits of error quite great. The most careful work is that of Elissafoff (*Zeitsch. Physikal Chem.*, 1912, **79**, 385) who considers the limits of error to be about 10 per cent. in his experiments. It will be seen from the following tables that the agreement is as good as can be expected.

In applying equation (10) or (11) it should be remembered that :

(*a*) Chemical action between the surface and the oppositely charged ion is not always negligible, and

(*b*) That the surface concentration is not always the same as that in the bulk of the liquid. Thus " adsorption " due to variation in surface energy in the sense of Gibbs' well-known equation is always possible.

The solid substances examined by Elissafoff are glass and quartz. We shall assume that the charge of the surface is due to the fixation of " hydroxyl ions " by chemical affinity.

From equations (11) and (12) we get

$$1-\theta_2=k_0c.\frac{n_2-n_1}{n_1}\theta_2+k_0c.\theta^2{}_2 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For hydroxyl ions $n_1=1$ and putting n_2 equal to 1, 2, 3, 4 successively we get the following equations for the adsorption of oppositely charged ions of valency 1, 2, 3 and 4 respectively.

$$k_0c\theta^2{}_2+\theta_2-1=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13A).$$
$$k_0c\theta^2{}_2+\theta_2(k_0c+1)-1=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13B).$$
$$k_0c\theta^2{}_2+\theta_2(2k_0c+1)-1=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13C).$$
$$k_0c\theta^2{}_2+\theta_2(3k_0c+1)-1=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (13D).$$

There is only one unknown constant in these equations. For comparison the values of θ_2 calculated by Elissafoff from an empirical equation is also given. The unit of concentration is taken to be 10^{-4} gram-ion per litre.

* *Kolloid. Zeitsch.*, 1909, **4**, 56.

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TABLE 5

Electrolyte—sodium chloride $k_0 = \cdot 0076$.

Glass capillary concentration.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22·5	43	43·4	42
68	37	36·4	34
136	31	30·6	29
225	26	26·4	26
2240	8	10·6	10
4500	5	7·8	5

TABLE 6

Glass

Electrolyte—potassium sulphate $k_0 = \cdot 00875$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
22	41	42·8	38
67	36	35·2	32
134	27	29·5	29
224	26	25·2	26
470	23	19·4	22
800	21	15·7	19
4000	8	7·7	10
7900	5	5·6	7

TABLE 7

Glass

Electrolyte—silver nitrate $k_0 = \cdot 059$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13A).	50 θ_2 (Empirical equation).
4	42	41·2	39
7	35	37·3	35
10	32	34·5	34
20	29	28·6	30
50	27	21	25
1000	9	5·8	8

TABLE 8

Glass

Electrolyte—barium chloride $k_0 = \cdot 0163$.

C.	50 θ_2 obs.	50 θ_2 (Eqn. 13B).	50 θ_2 (Empirical equation).
2·2	47	46·7	—
4·4	46	44	—
6	41	42	39
22	28	31·5	30
110	15	15	20

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TABLE 9

Glass

Electrolyte—uranyl nitrate $k_0 = \cdot 0168$.

C.	$50\,\theta_2$ obs.	$50\,\theta_2$ (Eqn. 13B).	$50\,\theta_2$ (Empirical equation).
3·5	52	—	—
7	45 (38)	41·1	39
10·5	38	38	36
14	36 (32)	35·4	33
28	29	28·5	27
56	23	21·3	21
112	14	14·5	15
140	13	12·6	13
238	5	8·7	9

The results of a second determination are given in brackets. For a concentration of 3·5 instead of a decrease a rise had been observed. These and other instances illustrate that the limits of error are considerable.

TABLE 10

Glass

Electrolyte—nitric acid $k_0 = \cdot 059$.

C.	$50\,\theta_2$ obs.	$50\,\theta_2$ (Eqn. 13A).	$50\,\theta_2$ (Empirical equation).
8	45	36·1	—
20	29	29·6	30
34	26	25	26
60	21	20·4	20
100	16	16·9	16

TABLE 11

Quartz

Electrolyte—potassium nitrate $k_0 = \cdot 01$.

C.	$50\,\theta_2$ obs.	$50\,\theta_2$ (Eqn. 13A).	$50\,\theta_2$ (Empirical equation).
8	48	46·6	—
28	43	40·6	43
68	33	34	33
120	28	29	26
390 (?)	10	19	13

TABLE 12

Electrolyte—calcium chloride $k_0 = \cdot 043$.

C.	$50\,\theta_2$ obs.	$50\,\theta_2$ (Eqn. 13B).	$50\,\theta_2$ (Empirical equation).
1·6	43	44·4	44
4·3 (?)	28	37·7	36
8·1	32	31·9	31
13·5	28	26·5	27
29·5	20	18·3	21
82 (?)	19	9·6	12

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Aluminium and thorium salts are hydrolysed to a large extent in such low concentrations as have been used by Elissafoff. The "hydroxide" has a positive charge in the colloidal state. Positively charged colloids can neutralise the charge of negatively charged colloids and equation (13) can no longer be applied.

From Table 7 we find that "silver nitrate" has a greater neutralising power than other monovalent ions. This should be attributed to chemical forces. Equation 13 holds good for the limiting case when there is no chemical attraction. In case of chemical action "W" as given in equation (1) no longer represents the stability of the adsorption of the ion. We can, however, put the energy required to separate the ion from the surface as equal to "W + B," where "B" is a measure of the chemical affinity acting on an ion. The form of the equation thus remains the same as in (13).

TABLE 13

Ions.

	$Na^{\cdot}$	$K^{\cdot}$	$Ag^{\cdot}$	$H^{\cdot}$	$Ca^{\cdot\cdot}$	$Ba^{\cdot\cdot}$	$UO_2^{\cdot\cdot}$	Surface
$k_0 \times 10^3$	·76	·87	5·9	5·9	x	1·63	1·68	Glass.
(Eqn. 13).	—	1·0	—	—	4·3	—	—	Quartz.

A discussion on the values of k given above is not possible unless we know "x" in Equation (1). If "x" has such a value that $-W/k.T$ for a univalent ion is less than 0·2, then $e^{-W/kT}$ for a divalent ion will be only slightly different from that of an univalent ion. In this case "k_0" in Equation (10) will be proportional to $n_z.u$, when n_z and u denote the valency and the mobility of the ion respectively. For the three ions $H^{\cdot}$, $K^{\cdot}$ and $Na^{\cdot}$, "k_0" is approximately proportional to their mobilities, *cf.* equations 10 and 13 (*a*).

Considering the simplifying assumptions made and the experimental difficulties involved, the agreement is as good as can be expected. The neutralisation of the charge of a colloidal particle by electrolytes is thus mainly the result of electrical "forces."

At the surface, however, the oppositely charged ions which are attracted are subject to the chemical affinity of the surface atoms. The order of adsorption deduced from Equation (10) will not hold for these cases. The order will be determined by the chemical affinity of the surface atoms. The alkali metal cations conform best with the theoretical series. This is in agreement with the fact that they have the least pronounced tendency to form complex "ions," to enter into combination with other elements to form "groups" and to form insoluble salts—all these facts point to their being least affected by "chemical affinity." Their chemical activity is simply due to their tendency to pass into "ions."

SUMMARY

1. The charge of a number of suspensoids has been traced to the adsorption of a common ion. The nature of the chemical forces to which this adsorption is due has been defined.

2. The effect of the electrical charge of a surface (due to the disorption of ions) on "ions" of opposite sign has been theoretically investigated for the case when chemical action does not take place between the surface and the "ion." It has been shown that the 'electrical" forces are sufficiently strong to account for adsorption.

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The stability of the adsorption of an ion of opposite sign by electrical forces has been given a quantitative form assuming that the charge of the surface consists of "ions" which can be treated as "point" charges widely separated from each other. Actual calculations justify this assumption.

3. The reversal of the charge by electrical adsorption has been discussed.

4. The following series of the order of adsorbability of cations by a negatively charged surfaces has been deduced from the theory

$$Th > Al > Ba > Sr > Ca > Mg > H > Cs > Rb > K > Na > Li.$$

5. This is the order of the precipitating power of these ions for a number of suspensoids of widely different chemical properties.

6. Equations deduced from the theory satisfactorily agree with the experimental observations of Elissafoff on electro-endosmose.

7. The chemical affinity of the surface atoms is not always negligible. For this reason the series given in paragraph 4 cannot be expected to hold in all cases. Equation (10) is applicable to this case also and retains the same form.

My best thanks are due to Professor F. G. Donnan, C.B.E., F.R.S., for his kind interest and advice, and to my friend Dr. J. C. Ghosh.

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ELECTRICAL THEORY OF ADSORPTION

BY

W. HARRISON, M.Sc., F.I.C.

The paper by Mukherjee dealing with the development of Langmuir's theory of adsorption is of considerable interest and importance and leads to some new ideas.

Recent work has shown that all atoms consist of positively charged nuclei associated with or surrounded by negatively charged electrons. Crystals have been shown to consist not of molecules bound together by some unknown chemical force, but of atoms held together by electrical forces. While there are examples such as that of alumina crystals, in which atomic groupings which might be considered as molecules are arranged in a regular manner, the distribution of electrons cannot be the same in any such grouping isolated from the crystal as within the crystal itself. Within the crystal the electrons are arranged so as to bind the atoms together in three dimensions. At the surface of the crystal, the electrons must be arranged to hold the atoms together in two dimensions, hence they are able to rearrange themselves for the accommodation of other atoms not necessarily the same as those already present. The formation of crystals with alternate layers of ammonia, alum and chromium potash alum by successive growth in solutions of the two compounds illustrates the above point. It is thus clear that a new surface may be formed by contact of a crystal with a solution.

There seems no reason to limit this argument to crystals where the atoms are oriented and the electric forces distributed so as to give strong combination. It will apply, and perhaps more correctly, to non-crystalline substances where the irregular orientation of atoms allows greater freedom for the rearrangement of electric forces.

Physicists having proceeded so far with the electrical explanation of chemical phenomena it appears to the writer unnecessary to go back to chemistry for the explanation of an electrical phenomenon.

It is not necessary, for instance, to assume that the electric charge at the surface of an adsorbent is due to chemical combination of the adsorbent with the ion. It is, of course, known that for most suspensoids the charge is of the same sign as that on the ion the substance has in common with the stabilising electrolyte, but stabilisation also occurs where there is no common ion, in which case the charge depends on the nature of the adsorbent and of the ions present. The colloidal metals form examples of this kind.

It is clear that the electrical equilibrium between two substances of different degrees of ionic or electronic saturation must necessarily be different from the equilibrium of electric charges at either of the two surfaces when not in contact, hence when contact occurs there will be a redistribution of electrical forces resulting in a difference of electrical potential.

In a solution electrical charges are always associated with ions, hence the above argument in no way modifies the equations of Mukherjee.

Mukherjee is of the opinion that the collisions of ions due to osmotic forces are comparatively negligible, and that the ions of the same sign as the colloid have very little influence. It is, of course, obvious

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that when the charge becomes neutralised the osmotic forces do come into play. The probability that a particular point on the contact surface becomes neutralised is the probability that an ion of opposite sign becomes fixed. This is also the probability that osmotic forces come into play at that particular point. The magnitude of this probability $1 - e^{-W/KT}$ is by no means small as will be seen from Table 2 of Mukherjee's paper, moreover it increases with the valency of either or both of the ions. In general, the effect of polyvalent ions is greater than that of monovalent ions, hence it is to be expected that a polyvalent ion of the same sign will increase the electric charge.[1] This was found to be the case by the writer when making experiments with cotton.

The electric charge had the following values in N/1000 solutions of salts :—

NaCl	Na_2SO_4	Na_3PO_4	NaOH
·0183	·0219	·0240	·0306

The anomalous effect of NaOH is undoubtedly due to the great mobility of OH ions.

The equation 13A of Mukherjee applies very well to some experiments made by the writer in 1912 (*Journ. Soc. Dyers and Cols.*, **27**, 279, 1911 ; **34**, 91, 1918).

Cotton—Hydrochloric acid solution

Concentration.	Observed E.M.F.	Calculated 13A.	Calculated empirical equation. $E = \cdot0081 \log C - \cdot0157$.
	Volts.		
1×10^{-4}	·0168	·0168	·0167
$2{\cdot}5 \times 10^{-4}$	·0138	·0136	·0135
5×10^{-4}	·0111	·0110	·0110
1×10^{-3}	·0085	·0085	·0086
$2{\cdot}5 \times 10^{-3}$	·0055	·0059	·0053
5×10^{-3}	·0028	·0044	·0029
1×10^{-2}	·0016	·0032	·0005
	Maximum	- ·0220	

With cotton and aluminium sulphate the results calculated from concentration were quite out of relation with the observed results, but when calculated from conductivity by equation 13, substituting 2 for n_2 and 3 for n_1, the results were much nearer to those observed.

Cotton—Aluminium-Sulphate Solution

Concentration.	Conductivity.	Observed E.M.F.	Calculated 13.	Calc. Empirical. $E = \cdot0064 \log K + \cdot0219$.
1×10^{-4}	$1{\cdot}44 \times 10^{-5}$	·0092	·0092 (92)	·0091
2×10^{-4}	$2{\cdot}37 \times 10^{-5}$	·0078	·0072 (68)	·0077
5×10^{-4}	$5{\cdot}4 \times 10^{-5}$	·0055	·0045 (38)	·0055
1×10^{-3}	$9{\cdot}8 \times 10^{-5}$	·0036	·0030 (24)	·0037
2×10^{-3}	$16{\cdot}2 \times 10^{-5}$	·0025	·0020 (15)	·0024
		values between		
5×10^{-3}	$32{\cdot}3 \times 10^{-5}$	$-\cdot0020$ and $+\cdot0016$		
1×10^{-2}	$56{\cdot}5 \times 10^{-5}$	$-\cdot0075$ and $+\cdot0043$.		

The values in brackets are calculated from 13 C.

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The writer considers the double layer as consisting of a surface of rigidly fixed atoms under continuous bombardment of positively and negatively charged ions, any particular point on the rigid surface becoming in turn negative, neutral and positive, these conditions arising in any order. The observed contact difference is the average effect of these conditions. Where several kinds of atoms are present in the solution the average number of any one of them at the surface will depend on their concentration, valency and mobility.

The variation of contact difference from negative to neutral and positive was observed with cotton and aluminium sulphate near the neutral point. These variations occurred during the same experiment, the readings being direct measurements of E.M.F.s developed by filtration under pressure.

[1] This point would be covered by putting $n_2 = 1$ and $n_1 = 2$ or 3 in Mukherjee's equation No. 13.

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COAGULATION OF INORGANIC SUSPENSIONS BY EMULSOIDS

BY

WILLIAM CLAYTON, M.Sc.

The mutual precipitating action of two oppositely charged colloidal sols has been investigated particularly in the case of the mutual precipitation of dyestuffs and also as regards the influence of certain organic colloids on basic and acidic dyestuffs. The general law deduced from such work is to the effect that oppositely charged colloids precipitate one another only when present within a certain range of concentration ratios, and only then if adsorption takes place.[1]

The precipitation of suspensions by electrolytes has also been extensively studied and instances are also recorded where a *non-electrolyte* like urea can effect the coagulation of certain colloids. The case of the precipitation of suspensions by emulsoids, however, is very vague, and in fact it is usual to find that "water-peptisable colloids like gelatin, gum arabic, dextrin, soap, or saponine, will peptise many precipitates, and they are often called protecting colloids because they prevent the agglomeration and consequent settling of finely-divided precipitates."[2]

The present paper describes experiments in which several exceedingly stable inorganic suspensions were, with remarkable rapidity, completely precipitated by small amounts of emulsoids, even though in certain cases the electric signs of the two colloids were identical.

A novel feature, too, was the fact that in every instance the added emulsoid solution causing precipitation was a frothing one, *i.e.*, capable of lowering the surface tension of water.

The more detailed results have been carried out with a stable suspension of an inorganic solid* in dilute HCl, which was very rapidly precipitated by a starch solution, a clear supernatant liquor being soon left above a heavy coagulum. The suspensions investigated contained 10 per cent. of solid and only 0·025 per cent. starch was required.

As one gradually adds the starch solution, stirring continually, a point is very suddenly reached, when the suspension clots into larger particles, which on ceasing stirring, sink very quickly indeed.

A suspension of the solid in pure water is also precipitated by a solution of starch in the same manner. This is inexplicable so far, because in water alone both the solid and starch are negatively charged. (*See* Table 1.)

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* Owing to commercial reasons, the name of this particular substance cannot be divulged. The solid was unaffected by heat, and in boiling water did not undergo change of any kind. The effects described in this paper cannot be attributed to any chemical change or reaction on the part of the solid substance.

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TABLE 1

Cataphoresis Experiments

Substance.	Medium.	Charge on Substance.	Substance migrated to
" Solid "	Pure water	— ve	Anode.
,,	Dil. HCl	— ve	,,
Starch	Pure water	— ve	,,
,,	Dil. HCl	+ ve	Cathode.
,,	Dil. NaCl	— ve	Anode.
" Solid B "*	Pure water	— ve	,,

In the case where starch precipitates in acid solution and where the charges are opposite, the small quantity of starch required to effect precipitation is in itself very strange, viz., 0·0025 per cent. of the total solid present.

The previous treatment of the starch is also important. If it is brought into solution by boiling with dilute alkali, its precipitating efficiency is nearly doubled. In actual practice the starch was boiled for 10 minutes in 0·3 per cent. NaOH to make a 1·75 per cent. solution. (In works' practice, this small amount of NaOH had practically no influence on the amount of HCl present.)

It was found that starch made up in alkaline solution precipitated the suspensions independently of temperature. Neutral starch solutions behaved unsatisfactorily as the temperature of the suspension was raised, whilst starch solutions made up in dilute acids were the least suitable for precipitating hot suspensions. (*See* Table 2.)

TABLE 2

Coagulation by the Use of Various Starch Solutions at Different Temperatures

All Starch Solutions 0·5 per cent. and all boiled for 10 minutes.

Starch.	Nature.	Temperature of Suspension.	Ratio of Starch to Solid.
Rice	Neutral	16° C.	1 : 176
,,	,,	94° C.	1 : 95
,,	Alkaline (0·5% NaOH)	11° C.	1 : 250
,,	,,	45° C.	1 : 250
,,	,,	87° C.	1 : 250
Maize	Neutral	16° C.	1 : 125
,,	Alkaline (0·5% NaOH)	16° C.	1 : 256
,,	,,	94° C.	1 : 222

Inspection of the Table shows that whilst rice and maize starches have different precipitating powers in neutral solutions at 16° C., their alkaline solutions have practically the same efficiency and behave independent of the temperature.

* This was another solid, entirely different from the first investigated, and its aqueous suspension was readily flocculated by starch dissolved in pure water.

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Other substances investigated were tannin, dextrin, milk, egg albumin, urine, beer and stout—all frothing solutions. With the exception of tannin, all caused coagulation of the suspension in dilute HCl, though a time factor of about one hour was noticed in the case of milk and egg albumin. Urine is an excellent flocculator, being rapid in action, and giving a precipitate of small bulk, in contra-distinction to the large "flocks" present in a precipitate due to starch.

Barium sulphate, china clay, talc powder, tin ore slimes, and basic magnesium carbonate, all in sludge states, have also been flocculated by starch solutions, but the exact relationships holding have not been finally settled. Further work is in progress, particularly with regard to basic magnesium carbonate.

Discussion

The precipitation of suspensions by electrolytes is now believed to be due more to selective adsorption of ions than to the existence of electrical charges of opposite signs; also, in general, the colloid adsorbs ions of opposite charge to its own, and the more so the higher the valency.

Here, however, are instances wherein it is difficult to find evidence for the electrical neutralisation view of coagulation; (non-electrolytes in fact, have been very successfully employed) because in certain cases (*e.g.*, starch and "1st solid" in water; starch and "2nd solid" in water), coagulation is effected even though the colloid charges are of the *same* sign.

The difficulty is still further increased by the fact that the coagulants are essentially substances which lower the interfacial tension. Quoting Lewis :—[3]

> "Let us consider substances which lower the surface tension of water, and the interfacial tension between the disperse phase and the medium. The lowering of tension leads of necessity to positive adsorption. Further, if the interfacial tension between the disperse phase and the medium be lowered by the added substance we would *not* expect coagulation to occur, for the total surface energy is now less than it was before. This is in agreement with Donnan's theory of emulsification, and is, in fact, the basis of Bredig's theory of the stability of colloid solutions. But the experiments on suspensions to which reference has been made show that coagulation is actually brought about by substances which lower the interfacial tension. We have here, apparently, a direct contradiction of our previous conclusion."

These results have been brought forward in the hope of inducing discussion on what for the present, remains a very strange series of results, quite unexpected on theoretical considerations.

[1] Bancroft, *Brit. Ass. Colloid Rept.*, II., p. 13, 1918.
[2] *Ibid., loc. cit*, p. 4.
[3] *System of Physical Chemistry*, Vol. I., 2nd ed., p. 365.

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SOME OBSERVATIONS ON PEPTISATION AND PRECIPITATION

BY

N. G. CHATTERJI AND N. R. DHAR

In his article on peptisation and precipitation, Bancroft (Second B.A. Report on Colloid Chemistry, 1918, p. 2) enumerates a large number of cases of peptisation. We have reinvestigated some of these reactions and come to the conclusion that in several cases the observations are not accurate. Thus we have found that silver chloride, silver chromate, and calcium silicate are not peptised in presence of a concentrated solution of cane sugar. What actually takes place is that, in presence of a concentrated solution of cane sugar or glycerine, the precipitate does not come down immediately. It only does so on keeping for some time. But if it is centrifuged and specially a little diluted, the precipitate settles down at once. It therefore appears doubtful whether peptisation at all takes place in these cases. True peptisation cannot give any precipitate when centrifuged in this way.

We have been successful in bringing about peptisation of a large number of hydroxides by means of glycerine, concentrated solutions of cane sugar or grape sugar. Thus the hydroxides of iron, nickel, thorium, mercury, cobalt, &c., have all been peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerine or sugar. In the case of uranium and gold, ammonium hydroxide should be used instead of caustic soda. In none of these cases could any trace of sedimentation be observed even after vigorous centrifuging. One curious fact in this connection seems to have remained unnoticed. It is generally recognised that a substance which can peptise another during the formation of the latter may not be able to do so when once the substance has been formed. We have now observed that not only is the above true, but that peptisation can only be brought about if the alkali hydroxide is added to the mixture of the salt solution and glycerine. On the other hand, precipitation at once takes place if the solution of the salt is added to the mixture of glycerine and alkali hydroxide. Peptisation does not seem to take place in the case of antimony hydroxide, copper fluoride or barium sulphate.

A reference to the literature on the subject of peptisation shows the confusion that exists in this branch of chemistry. The nature of the solutions obtained by dissolving aluminium hydroxide, for example, in alkali hydroxides has been the subject of much discussion. The literature on the subject puts forth evidence in support of both the peptisation and chemical combination views. We have tried to solve the problem systematically by finding out whether any change in electrical conductivity of a solution of caustic alkali takes place when any of the hydroxides is dissolved in it. Incidentally, we have investigated the solubility of the hydroxides of copper, zinc and cadmium in ammonia. We have found that a great increase in the conductivity of the ammonia solution takes place on dissolving these

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hydroxides. In this connection, it is interesting to observe that the cobalt-ammonium bases and the chromium-ammonium bases obtained by the double decomposition of a chloride of cobaltammine or chromiumammine by silver hydroxide are fairly strong bases (Cf. Dhar, *Proc. Akad. Wetensch*, Amsterdam, 1920).

In the case of the action between sodium hydroxide and the hydroxide of copper, chromium, lead, zinc, aluminium, mercury, the following results are obtained. The conductivity of a solution of caustic soda did not appreciably change on the addition of hydroxides of chromium, aluminium, lead, mercury, whilst in the case of zinc the resistance of the caustic alkali solution appreciably increased when zinc hydroxide was dissolved in it. Hence we can conclude that the solutions of aluminium hydroxide, chromium hydroxide, lead hydroxide, mercury hydroxide and copper hydroxide are cases of true peptisation and not of chemical combination. On the other hand, in the case of zinc hydroxide, we get more of chemical combination than of peptisation. Or, in other words, the major part of the hydroxides of aluminium, chromium, copper, lead and mercury exists in sodium hydroxide solution as a colloid, whilst the major part of zinc hydroxide remains as a zincate.

Bentley and Rose (*Jour. Amer. Chem. Soc.*, 1913, **35**, 1490), from their experiments, were led to the conclusion that freshly prepared aluminium hydroxide dissolves in dilute acetic acid to form a colloidal solution. If this be true, our conductivity experiments ought to show no change in the conductivity of the acetic acid solution when aluminium hydroxide is added to it. But if an acetate is formed, the conductivity ought to increase considerably, for acetic acid, being a weak acid, has small conductivity, but its salts are good conductors. As a matter of fact, we have found that the conductivity of an acetic acid solution does not change appreciably when freshly precipitated aluminium hydroxide or ferric hydroxide or chromium hydroxide is dissolved in it, whilst the solution of zinc hydroxide in acetic acid causes a great increase of conductivity. Hence we can infer that the hydroxides of aluminium, chromium and iron become peptised in acetic acid, whilst zinc hydroxide mainly forms zinc acetate with acetic acid. These results are corroborated by the fact that zinc hydroxide is a much stronger base than ferric, aluminium or chromium hydroxide.

We have already mentioned the peculiar behaviour of the products obtained by mixing together a metallic salt (capable of forming an insoluble hydroxide), ammonium or alkali hydroxide, and glycerine or a concentrated solution of sugar. We get or do not get a precipitate of the hydroxide according as we add the salt solution to a mixture of glycerine and hydroxide or the hydroxide to the mixture of the salt and glycerine. The clear solutions obtained in the latter case may be either due to the formation of a soluble compound of the hydroxide with glycerine or a colloidal solution of the metallic hydroxide. If a chemical compound is formed, new ions must appear, and the conductivity of the solution must differ from that of the one in which the metal gets precipitated as hydroxide, even though equal quantities of the reagents are taken in both the cases. But if the clear solutions are formed on account of the peptisation of the hydroxide in glycerine, there is, from the ionic point of view, no difference in the nature of the two solutions, and hence there should be no difference in conductivity of the two solutions.

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Here are some experimental results :—

(1) *Cobalt nitrate, glycerine, and caustic soda.*

Solution in the Cell.	Specific Conductance.
(*a*) Cobalt, nitrate glycerine and caustic soda—no precipitate.	·107
(*b*) The same precipitated	·107

(2) *Nickel chloride, glycerine, and caustic soda.*

(*a*) Clear solution	·094
(*b*) Precipitated solution	·094

(3) *Mercuric chloride, glycerine, and caustic soda.*

(*a*) Clear solution	·054
(*b*) Precipitated solution	·053

4) *Ferric chloride, glycerine, and ammonia.*

(*a*) Clear solution	·0053
(*b*) Precipitated solution	·0053

(5) *Uranium nitrate, glycerine, and ammonia.*

(*a*) Clear solution	·0021
(*b*) Precipitated solution	·0021

(6) *Gold chloride, glycerine, and ammonia.*

(*a*) Clear solution	·0014
(*b*) Precipitated solution	·0014

We find from the above that the conductivities of the two solutions are the same, and hence the ionic conditions of the two liquids are identical. We can, therefore, say with confidence that the clear solution is *not* due to the formation of any soluble complex, but only a peptised solution of the hydroxide. That they are really peptised solutions is further shown by the fact that a slight rise in temperature brings about a precipitation of the hydroxide, the same change also taking place if the solutions are kept for some hours.

When an alkali hydroxide is added to a solution of a copper salt, a blue hydroxide of copper is precipitated, which on warming becomes black, due, probably, to the formation of a compound less hydrated. But if during precipitation a trace of the copper salt remains undecomposed, the blue hydrate cannot be changed into the black one by any amount of boiling. The undecomposed salt cannot be completely removed by washing with cold water, and it seems probable that the undecomposed salt becomes absorbed by the blue hydroxide and stabilises it. Washing with hot water removes the undecomposed salt, and then the precipitate becomes black. We have observed that if to this black hydroxide a little of the copper salt be added and the whole boiled, a reversible change takes place and the blue precipitate reappears.

The next point for investigation was whether different alkali hydroxides have different actions on the stabilisation of the blue

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hydrate or not. In this connection certain striking observations were made. In order to get a rough quantitative idea, 1 c.c. of $\frac{N}{20}$ copper sulphate or copper chloride solution was taken in every case, a measured amount of the alkali of known strength was run in from a burette, and the total volume was made up to 40 c.c. in a boiling tube. The boiling tube was next put in a large beaker containing boiling water, and the time taken by each to turn black was noted. It must be emphasised that this being a case of reaction in heterogeneous medium, the results in some cases could not be exactly reproduced, but on the whole the following conclusions have been drawn from a large number of experiments :—

(1) The stronger the alkali, the quicker is the transformation from the blue to the black modification; thus taking equal concentrations of KOH, NaOH, $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, and aniline, it was observed that KOH blackened first. It was also observed that KOH transformed much more quickly than NaOH.

(2) The behaviour of calcium and strontium hydroxides is very peculiar. Here with an excess of alkali there is more than one stage at which a complete retardation of the change from the blue to the black form takes place. Thus, starting with a slight excess of the alkali, if we gradually increase the quantity, we find that the time taken to turn black gradually increases, reaches a maximum, and then decreases. With very large excess there appears to be a good deal of retardation.

Ammonium chloride and ammonium sulphate seem to retard this change, whilst ammonium nitrate and potassium chlorate are without any influence.

It is well known that in presence of an alkali, the blue freshly precipitated hydroxide of cobalt becomes pink. Now this change is exactly of the same type as the conversion of the blue copper hydroxide to the black variety. In this case also a trace of the undecomposed cobalt salt, nitrate, for example, gets absorbed by the blue hydroxide and stabilises it, and we cannot get the pink variety of cobalt hydroxide if there is a little undecomposed cobalt salt left. Just as in the case of copper, warming of the black variety with a little copper salt regenerates the blue variety, in the case of cobalt warming of the pink form with a little cobalt salt also regenerates the blue variety, but in the latter case the cobaltous hydroxide begins to be oxidised in presence of air.

All those salts which produce a hydroxide soluble in excess of caustic alkali, namely, salts of zinc, aluminium, tin, lead, &c, markedly retard the transformation of both the blue copper hydroxide to the black form as well as that of the blue variety of the cobalt hydroxide to the pink form. It seems probable that the presence of aluminium hydroxide, lead hydroxide, tin hydroxide, &c., in the colloidal state tends to peptise the cobalt hydroxide or the copper hydroxide.

Benedict (*Jour. Amer. Chem. Soc.*, 1904, **26**, 695) casually observed that if an excess of a caustic alkali be added to the solution of a cobalt salt, the blue hydroxide which is at first formed does not change into the pink variety if a nickel salt be present. The greater is the retardation, the greater the amount of the nickel salt originally present in the solution. Benedict did not give any explanation of this peculiarity, neither did he mention the action of other salts on

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the rate of transformation of the blue to the pink modification. The effect of the presence of salts like ferrous ammonium sulphate, zinc sulphate, manganese sulphate, ferric chloride, chromium sulphate, potash alum, nickel chloride, tin chloride, lead nitrate, cadmium chloride, copper sulphate, magnesium sulphate, calcium chloride, thorium nitrate, strontium nitrate and uranium acetate has been investigated, and it has been observed that only the nickel salt produces a remarkable retardation. The next to produce the greatest retardation seems to be a calcium salt, but there is a great fall in retardation from nickel to calcium. The transformation of blue copper hydroxide to the black variety is also retarded by nickel salts. It is interesting to note that though a soluble nickel salt added to a cobalt salt before the addition of the alkali retards the change of the blue to the pink form, the reaction is not reversed upon the subsequent addition of the nickel salt to cobalt hydroxide. Neither is there any effect when nickel hydroxide is added instead of a soluble nickel salt, though undoubtedly the hydroxide of nickel is formed when excess of alkali is added to a mixture of the salts of cobalt and nickel.

Many interesting cases of adsorption have been observed, we believe, for the first time. Thus, if to the solution of an aluminium salt excess of concentrated alkali is added, the hydroxide at first precipitated redissolves. Now if a few drops of ferric chloride are added, the precipitated ferric hydroxide collected and washed thoroughly with hot water. This ferric hydroxide is now treated with caustic soda and filtered. The filtrate is boiled with ammonium chloride, and a precipitate of aluminium hydroxide is obtained. This is explained by the fact that ferric hydroxide during its precipitation adsorbs some of the colloidal aluminium hydroxide which is not removed by washing with hot water. Similar results have been obtained with a zincate and ferric chloride, and chromium hydroxide in solution and ferric chloride. Again, if to a solution of chromium hydroxide containing an excess of alkali a few drops of magnesium sulphate be added, the precipitate of magnesium hydroxide is found to contain a good deal of chromium hydroxide which cannot be dissolved by sodium hydroxide.

Summary

1. Silver chloride, silver chromate, calcium silicate, cupric fluoride and barium sulphate when precipitated in presence of glycerine or concentrated sugar solutions are not peptised.

2. The hydroxides of iron, nickel, cobalt, thorium and mercury can be peptised by adding a caustic alkali to the solutions of salts of these metals in presence of glycerine or concentrated sugar solution. In the case of gold and uranium salts, ammonium hydroxide should be used instead of caustic soda. In these cases peptisation can only be brought about if the alkali is added to the mixture of the salt and glycerine, but precipitation takes place if the solution of the salt is added to the mixture of glycerine and alkali. Conductivity experiments support these results.

3. The major part of the hydroxides of Al, Cr, Pb, Hg and Cu when dissolved in sodium or potassium hydroxide exists as a colloid, whilst zinc hydroxide mainly forms a zincate, shown from conductivity experiments. Similarly the hydroxides of Al, Fe and Cr form colloidal solutions in acetic acid, whilst zinc hydroxide forms zinc acetate.

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4. The transformation of blue hydroxide of copper to the black variety and that of the blue hydroxide of cobalt to the pink form are changes of the same type, and are almost equally affected by different catalysts.

5. The hydroxides of Al, Cr and Zn respectively are adsorbed by ferric hydroxide when the latter is precipitated in presence of solutions of the hydroxides of Al, Cr and Zn in caustic soda.

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THE ABNORMAL CRYSTALLIZATION OF LEAD AZIDE BY PROTECTIVE COLLOIDS

BY

A. G. LOWNDES

Lead azide PbN_6 has been known for some years past to possess all the essential properties of a serviceable initiator of detonation. Both its preparation and manufacture are very easily carried out, all that is necessary being to add a solution of sodium azide to an equivalent quantity of either lead acetate or lead nitrate. In the manufacturing process the acetate is usually employed when lead azide is formed according to the following equation :—

$$Pb(CH_3COO)_2 + 2NaN_3 = PbN_6 + 2CH_3COONa.$$

In the laboratory the azide is prepared by running in equivalent solutions of sodium azide and lead nitrate from two burettes into a suitable receiver containing a little water.

Now, the history of preparation and also of the manufacture of lead azide has been a very checkered one. Explosions have been frequent and no very satisfactory cause has been found for them. It has been generally agreed, however, that these explosions are caused by the fracture of large crystals and, although I have reason to doubt this statement, the problem was at the time to produce the azide in such a way that large crystals, and also crystals that were likely to fracture, should not be formed. This problem was at the time being tackled by the research department of Nobel's Explosion Co., Ardeer Factory, Stenenston, Ayrshire, N.B., where I was employed at the time doing microscopic work.

Any one who is familiar with microchemical analysis knows that the *bête noir* of all such work is the presence of the slightest trace of a colloid on the microscopic slide which prevents the formation of the normal crystals by which the particular reaction is recognised. On hearing, therefore, of the azide problem, I suggested that the water of the receiver should be replaced by a $\frac{1}{2}$ per cent. solution of gelatin or dextrine. This was accordingly done by the Assistant Manager of Research, Dr. Weir.

The effect of adding the colloid can be seen by reference to the photomicrographs.

Fig. 1 represents a normal manufactured sample, and it will be seen to consist of large partially formed crystals which belong to the Rhombic system. These crystals are really far more solid than they appear, the thickness being considerable.

Fig. 2 simply represents one of these crystals under higher magnification.

Fig. 3 represents a laboratory preparation and shows very perfect crystals, one of which shows a very characteristic twin.

Fig. 4 represents a highly magnified crystal, the twinning of which has given rise to radiating appearance. This kind of crystal was supposed to be the highly sensitive one as it is very liable to fracture on being compressed.

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FIG. 1.—Normal manufactured sample.
Magnification 50 diam.

FIG. 2.—Normal manufactured azide.
Magnification 500 diam.

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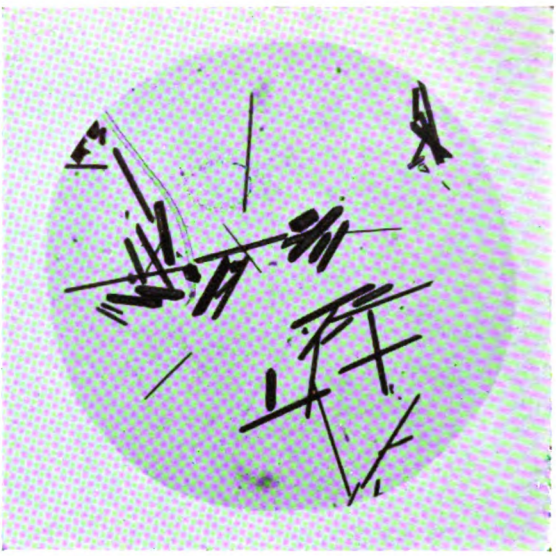

FIG. 3.—Laboratory preparation.
Magnification 50 diam.

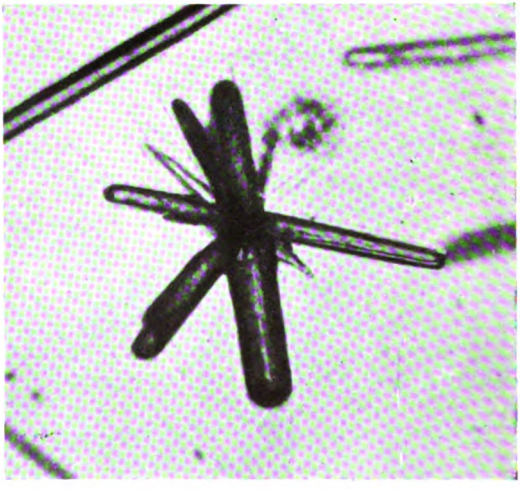

FIG. 4.—Laboratory preparation.
Magnification 500 diam.

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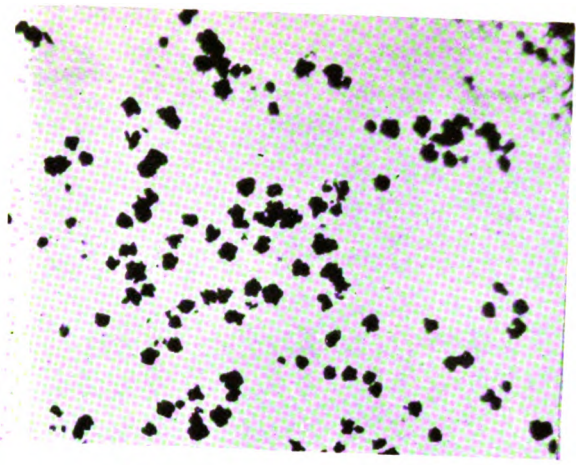

FIG. 5.—Magnification 50 diam.

FIG. 6.—Magnification 50 diam.

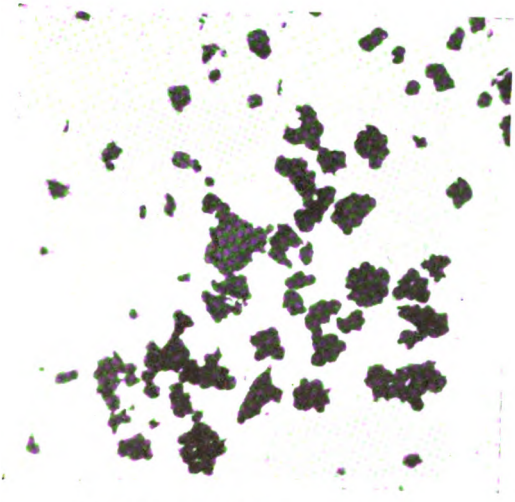

FIG. 7.—Magnification 50 diam.

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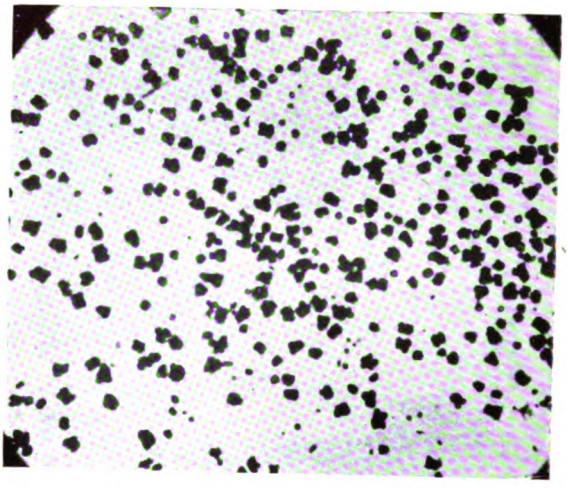

FIG. 8.—Magnification 50 diam.

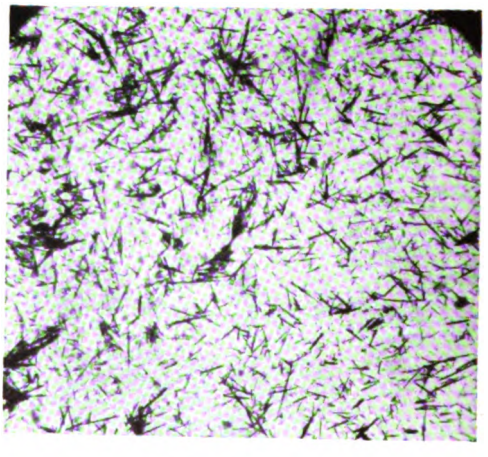

FIG. 9.—Magnification 50 diam.

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Figures 5, 7 and 8 represent the result of adding a colloid to the receiver solution. The products are seen to consist of rounded aggregates with little resemblance to the original crystals.

Fig. 9 represents the result of adding ferric chloride to the receiver solution. It will be noticed that the product is certainly crystalline and from a manufacturing point of view is a quite unsuitable product.

Fig. 6 represents a peculiar crystal that was formed when the receiver solution contained 0·5 per cent. ferric chloride acidified with glacial acetic acid.

It probably consists of a basic ferric azide as microchemical analysis showed it to contain iron.

The crystal was also shown to be insoluble in nitric acid. Further analysis was not carried out since it involved the separation by mechanical means of the crystals on the microscopic slide.

Not only was it essential to prevent normal crystallisation but it was necessary to produce the azide in a homogeneous form, and also in a form that would possess a low angle of flow in order to comply with the necessary conditions of filtration and the further loading of detonators. The necessary conditions were found for producing large quantities of the azide represented in Fig. 8.

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ON THE USE OF COLLOIDS IN ELECTRODEPOSITION OF METALS

BY

W. E. HUGHES, B.A. (CAMB.)

It has been stated that the employment of colloids in baths used to deposit metal electrolytically should be avoided. Any such general statement is regrettable, since it is unsupported by facts. The truth is that unless colloids, or substances which produce similar effects to those caused by colloids, are added to some solutions, the metals it is required to deposit from them cannot be obtained at all in a coherent and useful form. A typical example is the solution for lead deposition. In both the hydro-fluosilicic acid solution[1] and the perchloric acid bath,[2] colloids—glue and peptone, respectively—must be used. If they are not, the deposit will be crystalline, and cannot be obtained in any useful thickness. Again, whether essential or not, it is found that colloidal substances have been added with useful effect to many zinc baths. J. N. Pring and T. C. Tainton[3] use gum tragacanth; dextrin forms a constituent of many recipes; a small amount of organic substance (probably glue or gelatin) was found to be present in a very fine sample of zinc deposit, 0·3 to 0·4 inch thick, which lately came to the author from Australia; and L. W. Chapman, in his description of the zinc refining plant at Trail, British Columbia, states that "Glue is sometimes added to the solutions and produces smooth coherent deposits."[4] Further, it may be mentioned that gelatin or glue is sometimes added in very small amount to the nickel or acid copper solution in order to obtain a very smooth, hard and bright deposit. For certain purposes the addition is useful, since deposits can be thereby obtained which are of such a brightness that they require no buffing after removal from the plating tank, and hence the cost of "finishing" is saved.

The substance used need not always be of an organic nature. Aluminium sulphate, and, sometimes, caustic alkali (especially caustic soda) can, in some cases, be employed in a zinc or tin bath to produce results similar to those effected by colloids. W. D. Bancroft states[5] that tin salts added to the acid copper bath have a beneficial effect upon the deposit. Many other instances might be given.

It appears, therefore, that the use of colloids is not only not to be avoided, but that in many cases of both plating and refining solutions the employment of them makes it easier to obtain a smooth and coherent deposit, and in some cases they *must* be used in order to obtain a satisfactory deposit at all.

The cause of the beneficial effect of colloids and the like upon electro-deposited metal, considered from the plating or refining point of view, soon becomes apparent upon observation. The deposit, as formed in the absence of such substances, is obviously crystalline in almost all cases. Sometimes the crystals of the deposit are, so to say, *en masse*; sometimes they are isolated skeletons. In the former case, one has a useful, more or less homogeneous, deposit; in the latter case, no useful, coherent deposit is formed. Addition of substances of the kind mentioned causes, in many cases, a change which acts

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in the direction of diminishing the size of grain. The change is so extreme in some cases, for example, lead, that the deposit shows, on visual inspection with the naked eye, no sign of structure; it may even appear to possess a bright, polished surface, as in the cases of copper and nickel. Such macroscopic appearances imply hardness in the metal, and often brittleness. Lead is the only metal to form an exception to this association, so far as the author's experience goes. On microscopic examination, however, it is found that the deposit is really crystalline, even where the surface is bright and polished in appearance. The author has never succeeded in finding an instance where this was not so.

Although the change effected by colloids is easily observable in the diminution of the size of grain of which the deposit consists, the way—the *modus operandi*—in which that change is brought about is unknown. The scientific interest of this matter at once appears when it is recalled that, really, one is concerned here with the phenomena of crystallisation and the effect of colloids upon them. So far as pertains to electro-deposited metal, very little work has been done on the subject. R. Marc[6] and V. Kohlschütter,[7] working separately, and H. Freundlich and J. Fischer,[8] in collaboration, appear to be the only investigators who have seriously considered the matter at all in a scientific way. It is notable that these workers give differing views as to the causes that bring about the change in the structure of deposited metal resulting from the presence of colloids in the depositing solution. Freundlich and Fischer say that the change is due to adsorption: Kohlschütter believes that the colloids give rise to colloidal metal. One reason for the prevalent difference of view is that the facts are insufficiently ascertained. There is, in fact, a practically untouched field of inquiry here.

It is, therefore, suggested that on both the practical and theoretical sides, the subject of the use of colloids in solutions employed for the deposition of metals is one of interest and importance, and one to which attention may appropriately be directed during a discussion on the physics and chemistry of colloids and their applications.

[1] A. G. Betts, *U.S. Pat.*, 679, 824 (1901); *Eng. Pat.*, 1,758 (1901); *Met. and Chem. Eng.*, 1903, Vol. 1, p. 407.
[2] F. C. Mathers, *Met. and Chem. Eng.*, 1910, Vol. 8, p. 350; *Trans. Am. Electroch. Soc.*, 1910, Vol. 17, p. 261.
[3] *Eng. Pat.*, 7,255 (1911).
[4] *Chem. and Met. Eng.*, 1920, Vol. 23, at p. 231.
[5] *Trans. Am. Electroch. Soc.*, 1912, Vol. 21.
[6] *Zeit. f. Elektroch.*, 1913, Vol. 19, p. 431.
[7] v. V. Kohlschütter and H. Schacht, *ibid.*, Vol. 19, p. 172.
[8] *Ibid.*, 1912, Vol. 18, p. 885.

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DISCUSSION

Dr. W. R. Ormandy : I should like to make a few remarks on Mr. Mukherjee's paper, because I think it is one of the most important presented during this evening, in that it deals with some of the fundamental aspects of the broad subject under discussion. The question of the nature and origin of the charge upon colloidal particles is of fundamental importance, and it is unfortunate that, so far, a great deal of the work that has been done upon this subject has been carried out for the most part with exceedingly dilute suspensions, where the error introduced by the ever-present ionised impurities in the water employed may exert a very great influence. Much of the work upon the charge on suspensoid particles is based upon their rate of movement in an electric field. It is generally admitted that, in the absence of free ions in the liquid, there is no movement of the suspended particle in an electric field. It is not so widely realised that the suspended particle may itself carry on its surface a large amount of adsorbed material which could not be removed by any amount of dialysis, but which is set free in the ionised form, if the voltage employed during the measurement of the movement of the particles exceeds a certain limit. I do not think that the present explanation of the movement of suspended particles in an electric field is by any means complete. It seems to me desirable that, wherever possible, the investigations on adsorption and subsequent work on the rate of movement of the particles should be carried out on bodies which in the non-dispersed state are capable of easy microscopic examination, and which can be dispersed until they are beyond the range of microscopic examination. Further, the ideal material would be practically insoluble in water, or when in equilibrium with water would give to the water a constant and low conductivity. I believe that such a material is available in the form of certain types of clay, but for this purpose the china clays, which are essentially crystalline in structure, are not suitable. As at this late hour it is impossible to give the subject the consideration which it deserves, and as I have quite a lot of experimental work dealing with this matter which I hope to publish at an early date. I propose to use the opportunity of such publication for an extended discussion of the paper in question.

Prof. E. F. Burton (University of Toronto) (*communicated*) :

In regard to Prof. Mukherjee's reference to the variation in the coagulating power of ions with the concentration of the sol, I may report that there is now in print, to appear in an early number of the *Journal for Physical Chemistry*, an account of work by myself and Miss Bishop, of which the following is a summary :—

With solutions of (1) arsenious sulphide, (2) mastic, and (3) copper (Bredig), it was found that the variation in the coagulative power with the concentration of the disperse phase followed three laws :

(1) For univalent ions the concentration of the ion necessary to produce coagulation increases with decreasing concentration of the colloid—this increase being very marked with low concentration of the colloid.

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(2) For divalent ions the concentration of the ion necessary to produce coagulation is almost constant, *i.e.*, independent of the concentration of the colloid.

(3) For trivalent ions the concentration of the ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

This suggests that coagulation is not due merely to simple adsorption of ions, but may be affected by other conditions such as conductivity of the medium and the nature of the ion bearing the same charge as the particles. In particular, it is important to remember that, in the case of all coagulation experiments, when testing the coagulating power of monovalent ions, one always has present ions of the opposite sign of *equal* or *greater* valency, while, in like experiments on trivalent ions one always has present ions of the opposite sign of *less* valency.

Mr. W. Harrison (*communicated*) :

The observation of Clayton that starch, an electro-negative colloid, is precipitated by negatively charged substances such as china-clay, magnesium carbonate, &c., does not rule out the electrical theory of coagulation. In the first place, ordinary starch contains electrolytes which have a strong influence on its properties. (*Compare* Harrison, *J. Soc. Dyers and Cols.*; Samee and others, *Kolloid Chemische Beihefte*, 27, 84, 1911, and 32, 32, 1916; Vols. 3 to 8, 1911–16.)

The fact that alkali increases the coagulating property of starch is important, because starch forms an ionisable compound with caustic soda, and it is most probable that the positive ions from this compound is really responsible for the coagulation of the suspensions mentioned by Clayton.

Mr. J. N. Mukherjee (*communicated reply*) :

Regarding Dr. Ormandy's remarks that the applied voltage may " set free in the ionised form " electrolytes adsorbed on the surface of the colloidal particles, I am rather doubtful whether for the field strengths usually employed (3 to 4 volts per centimetre) there is any justification, either on theoretical or experimental grounds, for the suggestion. At any rate, the numerous observations on the decrease in the migration velocity for the same applied E.M.F. on the addition of electrolytes show conclusively that the electrically adsorbed ions of opposite charge are not set free from the surface by the electrical field. As it is not mentioned how the limiting voltages are arrived at and as their magnitudes are also not given it is not possible to discuss it any further.

I have seen the paper referred to by Prof. Burton (*J. Phys. Chem.*, 1920, **27**, 701–15). I would like to draw the attention of Prof. Burton to a paper by myself and Mr. Sen on the same subject (*Trans. Chem. Soc.*, 1919, **115**, 461–472) where exactly similar observations have been recorded and which has evidently escaped his notice.

We have further observed that for electrolytes with divalent cations (barium chloride) all the three influences mentioned above can be noticed (*loc. cit.*, p. 465, Table III.). The observations have been satisfactorily accounted for on the basis that we are dealing with two influences :—

(1) the effect of the distance between the particles as affecting their rate of mutual collisions—this factor was first pointed

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out by Woudstra in 1908, and v. Smoluchovski has since given a quantitative form.

(2) the change in the amount of colloid-liquid interface with consequent variation in the amount adsorped (*loc. cit.*, pp. 465–468) as originally discussed by Freundlich.

Only arsenious sulphide, copper sulphide, and mercuric sulphide sols were studied. It is interesting to note that mastic and copper sols also show the same effect.

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SECTION VI.—ELECTRIC ENDOSMOSIS AND CATAPHORESIS

INTRODUCTORY ADDRESS

BY

ALFRED W. PORTER, D.Sc., F.R.S., F.INST.P.

I.—ENDOSMOSIS

When a porous diaphragm separates two parts of a liquid through which an electric current is passing, the liquid is often seen to be flowing through the membrane, sometimes towards the anode, but usually towards the cathode. This is electric endosmosis. If a difference of level between the two sides is allowed to be set up the flow ultimately ceases. The phenomenon was discovered by Reuss[1] in 1808, and again, by Porrett[2] in 1828. It was studied by Wiedemann[3] and Quincke,[4] who observed that the effect is greatest when the liquid conducts badly; that the quantity of the liquid transported is proportional to the current and independent of the width and thickness of the diaphragm, at least, within the limits of their experiments. The amount transported depends not only upon the liquid but also upon the nature of the surfaces in the diaphragm.

On the other hand, when liquids are forced through tubes a difference in potential is set up. The two phenomena are correlative one to the other.

A mathematical discussion of these phenomena was given by Helmholtz,[5] who showed that both can be explained if an electrical double layer exists at the boundary between two substances, such as the liquid and the porous diaphragm.

Consider the case of a conducting liquid contained in a cylindrical tube. This is the simplest case, because everything will be symmetrical round the axis. For very slow motions the liquid moves in parallel lines (excepting near the ends), and consequently (for an incompressible liquid) the longitudinal velocity u at a given distance r from the axis has the same value from end to end of the tube.

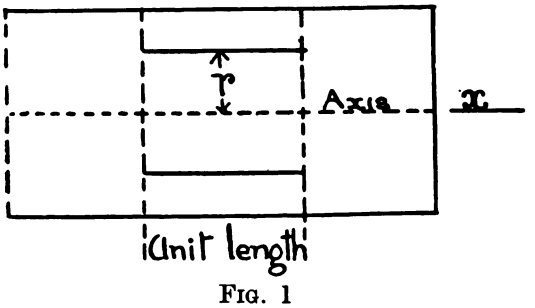

FIG. 1

Let a longitudinal voltage, $V_1 - V_2$, be applied so as to be uniform across the cross section. If there is a charge, q, *anywhere* in the liquid the force upon it is $-q\frac{\partial V}{\partial x}$. Select any cylinder of unit length and

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radius r and let q be the total charge within this cylinder. By the theorem of Gauss the charge q multiplied into $4\pi/K$ (K = dielectric constant) is equal to the total normal electric induction outwards from the surface of the cylinder, *i.e.*, since the electric force outwards from the curved surface is $-\frac{\partial V}{\partial r}$ and the curved area is $2\pi r$

$$-\frac{\partial V}{\partial r} \cdot K \cdot 2\pi r = 4\pi q. \quad - \quad - \quad - \quad - \quad (1)$$

Again, if a steady state of flow has been set up, mechanical equilibrium requires that the longitudinal force on the charge $-q\frac{\partial V}{\partial x}$ shall balance the force due to friction against the curved area or

$$-q\frac{\partial V}{\partial x} = -2\pi r\mu\frac{\partial u}{\partial r} \quad - \quad - \quad - \quad (2)$$

where μ is the viscosity of the liquid.

Eliminating q we obtain

$$K\frac{\partial V}{\partial r} = \frac{4\pi\mu}{-\frac{\partial V}{\partial x}}\frac{\partial u}{\partial r}.$$

Now the electric current ,C, is equal to

$$-\frac{\partial V}{\partial x} \cdot \frac{A}{\sigma}$$

where σ = specific resistance of liquid
A = cross sectional area of tube;
therefore

$$\frac{\partial V}{\partial r} = \frac{4\pi\mu A}{K\sigma C}\frac{\partial u}{\partial r}. \quad - \quad - \quad - \quad - \quad - \quad - \quad - \quad (3)$$

This equation is independent of the particular distribution of electric charge across the cross-section. If V_a and u_a are the potential and velocity at a point on the axis, and V_w and zero are the corresponding values for the tube wall, it follows that

$$V_a - V_w = \frac{4\pi\mu A}{K\sigma C}u_a. \quad - \quad - \quad - \quad - \quad - \quad (4)$$

It should be observed that μ, K, σ and C/A are all *specific* quantities.

The meaning of a double layer is that there exists near the surface of the liquid a distribution of electricity of one sign, while an equal quantity of opposite sign exists on the solid. We do not need to enquire too closely into how this charge in the liquid is distributed, provided that it is in the immediate neighbourhood of the surface; or, more precisely, provided that the distance of any of it from the surface is small compared with the radius of the tube. Equation 2 shows that wherever there is no charge, $\frac{\partial u}{\partial r}$ is zero; hence, in practically the whole tube u then is constant and equal to u_a. The total flow of liquid is consequently $u_a A = U$ (say). Hence, from (4)

$$U = \frac{K\sigma C}{4\pi\mu}(V - V_w) = \frac{KA}{4\pi\mu}\text{ long}^{l}\cdot\text{ voltage} \times \text{trans. voltage}. \quad - \quad (5)$$

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Here $V_a - V_w$, the transverse voltage, is the drop of potential across the double layer.

The assumptions made in this proof are identical with those made by Helmholtz; but the method of solution is much simpler and the conditions under which equation (4) holds are, I think, made clearer. In addition, the influence of the dielectric constant has been allowed for (Helmholtz took it as unity). This has been allowed for in the routine fashion, although with some diffidence. If it is to be taken as equal to the dielectric constant of the liquid as ordinarily measured, it would seem to require that the charge in the liquid is distributed over a thickness containing a fair number of molecules. This, of course, would be possible without equation (4) being invalidated thereby.

Horace Lamb[6] discussed the problem afresh, because he was dissatisfied with Helmholtz's application of the equation to thin layers of molecular dimensions. Instead of assuming that u and V vary continuously, he considers that finite slip occurs near the boundary between the liquid and solid. Instead of a friction per unit area at the boundary equal to $-\mu \frac{\partial u}{\partial r}$ he puts a force proportional to the discontinuity in the velocity at the surface He then confines his attention to the case where the charges are distributed over the surfaces of this discontinuity. I have put forward the proof given above in the hope that it also removes some of the difficulties in Helmholtz's proof.

To calculate the total charge on each face of the double layer, we are on much more uncertain ground. We return to equation (1), where it is given by

$$q = \frac{K \times \text{surface of layer}}{4\pi} \times \text{trans. slope of pot. at wall.}$$

If we write this slope as $\frac{V_a - V_w}{b}$ we define a *mean* thickness b of the double layer. This thickness is probably comparable with molecular dimensions. If it be assumed equal to the distance of two molecules apart in the liquid q can be determined after $V_a - V_w$ has been determined by equation (5) from endosmotic experiments.

But there is no certainty that this assumption is true, and the value of q is uncertain to the same extent.

II.—Cataphoresis

Similar double layers are formed at the surface of solid particles immersed in a liquid and relative motion of the particle and liquid takes place when an electric current flows through the liquid. The particle is usually considered to be non-conducting, but this will clearly not be so in the case of metallic suspensions.* Since, in these cases, the solid is easily moved, its motion relative to the liquid, regarded as at rest at some distance from the particle, can easily be observed. This motion is cataphoresis. It was examined by Quincke, and, later, in more detail, by Linder and Picton.[7] The motion follows from the double layer theory. If an equal opposite velocity to that of the particle is impressed on the whole system, the

* It may then, however, be coated with a non-conducting layer (of oxide, for example), which would make the particle effectively non-conducting. It is doubtful to what extent a colloidal metal is the pure metal.

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particle will be at rest while the liquid at a great distance will have a uniform motion, v. Let the gradient of potential driving the current also be uniform at a great distance and equal to G; both v and G being parallel to x. At a great distance the potential will be given by $V = -Gx$, whereas near the particle additional terms will enter, due to the disturbance introduced by the presence of the particle, which vanish at a great distance. When the motion is slow, the motion will everywhere be irrotational, and in this case can also be derived by differentiating a potential function ϕ and at a great distance $\phi = -vx$; whereas near the particle additional terms will enter, which vanish at a great distance.

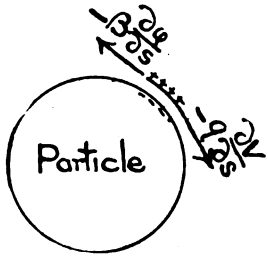

FIG. 2

Now if we follow Lamb in assuming a slip $u_0 = -\frac{\partial \phi}{\partial s}$ at the surface of the particle, the corresponding force due to friction on an element of unit area is $-\beta\frac{\partial \phi}{\partial s}$; the force on the charge on the element is $-q\frac{\partial V}{\partial s}$ and for steady motion $-\beta\frac{\partial \phi}{\partial s} - q\frac{\partial V}{\partial s} = 0$.

This condition is satisfied if we take $V/\phi = \beta/q$ everywhere.

Hence $\frac{G}{v} = \beta/q$ also.

But v is equal but opposite to the actual velocity of the particle, and G is the gradient of potential $-\frac{\partial V}{\partial x}$ in the undisturbed part of the field. Hence, if c is the current per unit area in this part

$$c = -\frac{1}{\sigma}\frac{\partial V}{\partial x} = \frac{G}{\sigma}$$

and therefore $-v = \frac{q\sigma c}{\beta}$.

The radial voltage at the particle is

$q \div$ capacity per unit area

$= q4\pi b/K$ approximately (for a thin layer), where b is thickness of the double layer.

Also, as before $\beta u_o = \mu\frac{\partial u}{\partial r} = \mu\frac{u_0}{b}$ whence

$-v = \frac{K\sigma c}{4\pi\mu} \times$ radial voltage in double layer. This is identical with the endosmotic equation, but with reversed sign.

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III.—Origin of the Double Layer

A few words only will be said here in regard to the origin of the double layer. The phenomenon is obviously an example of the preferential attraction of electrons to particular bodies. It is this preferential attraction (the "specific attraction" of Helmholtz) to which ordinary electrification by "friction" is due. The two opposite faces of the bodies in close contact become oppositely charged, thus forming what is, in reality, a double layer, the components of which can be separated by a separation of the bodies themselves. Very small changes in the surface are sufficient to reverse the direction in which the transferred charges go. Roughening a glass surface is sufficient to make it become the negative body against silk. Two pieces of thin celluloid, placed in juxtaposition and passed quickly between the thumb and forefinger, in such a way as to curve them strongly during the passage, become oppositely charged; the one which touches on its convex side becoming positive, as though electrons had "evaporated" or "dissolved" from it more easily. Similarly, between a solid and a liquid, Voltaic differences of potential are set up, being due to a passage of charged ions (*i.e.*, ions carrying electricity with them) across the interface. In this case the preferential attraction for the matter of the solid has to be considered as well as that for the electricity. Similarly, there is specific attraction causing "adsorption" at an interface; and the adsorbed elements may be charged. In endosmosis and cataphoresis we are only concerned with electrolytes, because it is essential that an electric current can flow. When the solid becomes positively charged it may be due to positive ions (either of H in the case of an aqueous solution, or of the cation of the solute) being attracted and forming a sessile layer around it; while the corresponding anions produce a negative region in the neighbourhood. These anions will be attracted to the sessile layer; but they will, no doubt, form a much more mobile region, because it will be more accessible to the shocks arising from the agitation of the molecules of which it is composed. It is for this reason that I have emphasised, in the proofs which form the main theme of this introduction, that the main conclusions do not depend upon the precise distribution of the charges in the liquid (*see* equation 4). The representation of the double-layer by two parallel sheets of charges is, of course, merely the result of the process of averaging which it is convenient to pursue in dealing with such complicated circumstances as those which exist in the body of a liquid.

In a paper to be communicated to this meeting by J. N. Mukherjee, the transitional character of this mobile layer is emphasised and deductions are made from it which seem to deserve very careful consideration.

Finally, it may be well to mention, that the potential-drops across the layer in the case of small particles may very likely be different from those observed at extended surfaces. I am not aware of any evidence on this point. The experiment with curved celluloid, quoted above, illustrates the possibility of the effect being different.

It is, of course, merely a special case of the influence of pressure—the pressure inside the particle being different from that outside

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Similar effects arising from the same cause are the variations, with pressure, of solubility and vapour pressure.

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References

(1) Reuss (*vide* Wiedemann).
(2) Porrett, *Pogg. Ann.*, **12**, 618 (1828).
(3) Wiedemann, *Pogg. Ann.*, **87** (1852), and **99** (1856); also Wiedemann's *Electricität*, ii, 166, *et seq.*
(4) Quincke, *Pogg. Ann.*, **113**, 513 (1861).
(5) Helmholtz, *Ann. der Phys.*, **7**, 337 (1879). *Memoirs London Phys. Soc.*, 1888 (translation).
(6) Lamb, *Brit. Ass. Rep.*, 1887, p. 495; *Phil. Mag.*, 5th S., **25**, 52 (1888).
(7) Linder and Picton, *J. Chem. Soc. Lond.*, **61**, **67**, **71**, **87**.

A bibliography containing 33 references is given in E. F. Burton's "The Physical Properties of Colloidal Solutions" (Longmans, Green & Co.). A summary of our present knowledge is given by T. R. Briggs, of Cornell University, in the Second Report on Colloid Chemistry, published, for the British Association for the Advancement of Science, by the Department of Scientific and Industrial Research (1919, 1*s.* 6*d.* net).

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SOME PRACTICAL APPLICATIONS OF ELECTRO ENDOSMOSIS AND CATAPHORESIS

BY

W. R. ORMANDY, D.Sc.

The number of industries which have arisen out of the deliberate application of the theoretical laws relating to electro endosmose and cataphoresis are comparatively few and there is not much progress to record since the issue of the second report on Colloid Chemistry which appeared in 1918.

The work, which has issued from the laboratory of the Elektro Osmose Aktiengesellschaft, still remains the largest contribution to this class of work. Undoubtedly the Schwerin patents applied to the purification of clay form one of the most interesting practical adaptations of the complicated physical laws dealing with colloids.

The history of the development may be described briefly as follows :—

First the discovery that suspensions of many clays could be so treated by a direct current of electricity as to bring about the deposition of the clay in a more or less dry state on a negative pole. It was found that all clays did not re-act and a second series of patents deal with the possibility of increasing reactivity of the clay particles to the electric current by adding traces of suitable electrolytes which were absorbed by the clay.

Further work showed that even with the addition of suitable electrolytes there were clays which were not amenable to electrical separation or at any rate not in a sufficiently pronounced degree to render the process commercially applicable. A third series of patents was taken out claiming the use of added colloidal substances which would be adsorbed by the clay, which colloidal substances were then capable of adsorbing the necessary electrolytes, and for this purpose such bodies as silicate of soda, humic acid (Casseler brown earth) and the like were employed. Count Schwerin was one of the first to realise the possibility of applying the comparatively new scientific discoveries relating to colloids to industrial purposes. So far as my knowledge goes, he was the first man to recommend the addition of electrolytes, with or without other colloids, to clay suspensions, with the object of converting the clay into the sol condition so that the sedimentation of the heavier impurities might take place. It is impossible by mixing a plastic clay with even a large amount of water to separate the bulk of the impurities without losing a lot of clay substance and without the use of an excessive amount of water. The free silica which is always present in clay is surrounded by clay in the gel form and the separation of this clay from the particle only takes place when suitable electrolytes are added so that the clay is peptised and separated from the silica.

The osmose machine applied to the separation of the suspended particles is an interesting example of the application of comparatively recent physical-chemical laws. In the preparation of the clay we make use of the laws of selective adsorption, of the influence of

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adsorbed colloids and finally of the directive effect of an electric current on a suspension of particles in the sol condition. On the anode of the osmose machine the negatively charged particles are deposited and the moment a film of these exists over the anode, brought about by cataphoresis, electro endosmose comes into action and the water in and around the clay is electrically driven through the capillary spaces resulting from the close contact of the clay particles deposited on the anode. It is interesting to note that the amount of moisture remaining in the clay attached to the anode is intimately related to the physical nature of the clay substance. If china clay is being worked upon it will be found that if sedimentation is carried out to such an extent that only 50 per cent. of the clay substance remains in suspension, so that only the finer particles of the clay remain, such a suspension treated on the osmose machine will give a product containing approximately 28/32 per cent. of water. If the china clay which has settled out be now remixed with water and passed through the osmose machine—that is, if we make use of the coarser clay particles only—the osmose machine will yield a product containing 35/40 per cent. of water. On the other hand, if similar experiments be carried out with a very plastic ball clay having much finer particles in the sol suspension, the osmose machine may deliver a product containing as little as 18 per cent. of water. It would appear as though the percentage of water in the clay delivered from the osmose machine were due in some measure to the fineness of the state of division in the sol state and to some extent also it is a measure of the plasticity.

In treating a very pure specimen of a well-washed English china clay by the osmose process, it has been found possible to deposit as much as 6,833 kilogrammes of dry clay substance with 11·8 kilowatt hours of current when working at 50 volts pressure..

It is interesting to regard this deposition of clay by direct electric current as though we were dealing with the deposition of copper from a solution of one of its salts. On the basis of the figures given above, we should have to assume that the quivalent weight of china clay was of the order of 700,000 and that where a given current would deposit 1 gramme of hydrogen or 31½ grammes of copper, it would deposit 700,000 grammes of clay. Needless to remark, these figures can only be obtained when working with a very pure clay and with water of very low conductivity.

It has been stated that the electro-osmotic process does not bring about any purification of the clay material in the actual osmose machine, but, whatever may be the position theoretically, the fact remains that in practice such a purification is brought about, as has been proved beyond all doubt at the laboratory of the Osmosis Company, Limited, by Mr. Lawrie, when working on tons of china clays and ball clays.

Peat

The application of the electro-osmose filter press to colloidal peat suspensions results in the removal of large quantities of water at a comparatively low cost in fuel; thus hydraulically mined peat, containing only 5 parts of dry peat substance in 100 parts of suspension, results in the removal of 85 parts of water from the 100 parts of mixture, with an expenditure of current which can be produced by the consumption of one-sixth of the resultant fuel. The ultimate drying of the product from the filter press containing

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1 part of peat to 2 parts of water is comparatively simple, but the difficulties attached to the use of the process are more largely mechanical. Unfortunately peat is generally found in comparatively thin layers, and owing to the small percentage of dry substance contained in the peat, the osmose plant would soon be far distant from the point where the fuel was being worked. It is obvious that the process lends itself particularly to application in countries where water-power is available for producing the necessary electricity.

Colloidal Silica

By passing an electric current through silicate of soda solutions it is possible to drive out the soda and leave the silicic acid behind, but this can only take place if diaphragms are employed which will permit of the soda ions passing out of the silicate of soda solution and will not permit of backwards way diffusion into the inner chamber. Years of experiments have resulted in the development of such diaphragms, and it is now possible to produce silica solutions up to 30 per cent. in strength, but the stability of these solutions diminishes as the concentration increases. It is interesting to note that the stability of these silica solutions has been found to increase with each step in progress which has been made, resulting in the more complete removal of the sodium salts. These silicic acid solutions of 5/10 per cent. strength have been largely used on the Continent for therapeutical purposes, and the strong solutions after polymerisation result in the formation of a gel, which, on drying, produces an inert highly electro-negative finely divided colloidal gel, which has proved to have extraordinary properties as an adsorbent for use on wounds. In the Third Report on Colloid Chemistry, page 123, there is a reference to a statement by W. Ostwald " that fresh colloids (particularly silica) will pass through a membrane, but after keeping a few days they will not pass through." It adds " there is no connection between the rate of diffusion through the membrane and the molecular weight." It has been found that the silicic acid solution produced by the electro-osmose process, at the moment of its preparation, has a molecular weight corresponding to the formula H_2SiO_3, and that the molecular weight increases steadily with the time, until with a 10 per cent. solution, after about 6 weeks, the molecular weight has reached something in the order of 60–80,000, and obvious separation takes place. If a 10 per cent. solution of silicic acid be kept in a vessel lined with paraffin wax, it is possible, by means of conductivity experiments, to determine the age of the preparation to within a few hours. It would seem likely, therefore, that the ability of new solutions to diffuse through a diaphragm is directly and closely connected with the molecular weight. No doubt Ostwald's less pure solutions polymerised to such an extent in a few days that they could no longer pass through a diaphragm.

Tanning

It would appear that a very great simplification has taken place in the plant now used for electric tannage of skins. Two factories in Germany are at present employing the process, and the chief claim made is that it permits of the utilisation of very dilute tanning liquors, with complete utilisation of the tanning material. It is further claimed that experiments have shown that it is preferable to complete the tanning for two or three days in the ordinary way in strong

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liquors, and that the current consumption is thereby reduced from 20–25 kilowatt hours per square metre of hide, when complete electrical tanning is employed, to 6 or 7 kilowatt hours per square metre when finishing in strong liquors is employed. Here, again, progress has resulted entirely from the discovery of suitable membranes for the enclosing of the anode and cathode.

Ore Separation

It has been found that if a finely ground ore be suspended in water, that in many cases it is possible to add traces of electrolyte which are selectively adsorbed. If such finely ground ore be allowed to fall through a column of water to which has been added the necessary quantity of suitable electrolyte, and if a current be passed through the water at right angles to the path of the falling particles, the charged particles are drawn on one side and fall into separate receptacles, bringing about concentration of the ore.

Iron ores occurring in clay deposits have been concentrated by the removal of the clay substance on the lines above described.

Anti-Diphtheritic Serums

It has been found that the anti-toxin contained in the blood serum of a horse is combined, for the most part, with the para-globulin, very little being combined with eu-globulin, and practically none with the fibrinogen. It has proved possible by using suitable diaphragms to separate from the anti-diphtheritic serum of the horse a pure para-globulin containing the bulk of the anti-toxin previously present in the serum. Such anti-diphtheritic globulin is free from amino acids, and from the decomposition products of the albumen bodies such as albumose and peptones, and bodies containing ferments such as katalase, enzymes and the like. Furthermore, it is claimed that the anti-diphtheritic product so prepared is free from toxon. It has been urged that anti-diphtheritic serum of a horse may, and probably does, contain toxins which have been combined in a weak way with anti-toxins, and that these compounds may split up in the human body with the setting free of toxins which may lead to, and be the cause of, the dangerous secondary symptoms which so frequently occur after serum injection. It is claimed that the electro-osmose process separates the toxon as such, as well as splitting the compound of toxin and anti-toxin with separation of the toxin. The resulting pure anti-toxin para-globulin has a concentration six to ten times that of the best horse serum.

Gelatine

By the use of diaphragms very similar to those employed for the separation of the constituents in serum, it has proved possible to prepare exceedingly pure gelatines from low grade gelatine, and even from glue. These gelatines are so pure that a 5 per cent. solution may be kept for weeks or months without any bacterial growth occurring therein, owing to the fact that the whole of the food material which is necessary for bacterial growth has been so entirely removed. Such gelatine is being prepared in this country, and is being tested for photographic and other purposes.

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Removal of Oil from Water

The electrical methods which are employed for the removal of oil from watery emulsions is really an application of cataphoresis. The oil globules are charged by adsorption of the inorganic salts present in traces, and pass to the anode.

Dewatering of Oils.—It is well known that many tars produced by distillation and many natural paraffin oils contain water in a state of emulsion which is very difficult to separate. Just as the application of direct current electricity has for some time been employed as above stated for the separation of oil emulsions from water, so similar electrical methods are used for the removal of the water particles forming the disperse phase in oil as a continuous phase. This application is very largely used in the Californian oilfields.

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The following contribution to this Section was received from **Professor Dr. H. Freundlich** (Berlin-Dahlem), in response to an invitation:—

THE EFFECTIVE POTENTIAL DIFFERENCE OF ELECTRO-OSMOSIS AND ALLIED PHENOMENA

BY

H. FREUNDLICH (Berlin-Dahlem)

The nature of the potential difference at work in electro-osmosis, kataphoresis and allied phenomena—which I group as electrokinetic—is not as yet fully understood. On the theory of *Helmholtz*[1] of the electron double layer we can satisfactorily represent the physical aspect of the processes. But the relation between this electrokinetic potential difference ζ and the ordinary *Nernst* potential difference ϵ, with which we deal so successfully in the theory of galvanic couples, is not by any means clear yet. We might best solve this problem by measuring simultaneously, at the same wall, both the potential differences ζ and ϵ. In the case of metals, for which ϵ is so well known, unobjectionable measurements of ζ are not easily obtained. The kataphoresis of metal sols is objectionable because we are doubtful as to the state of the surface of the metal (its oxidation, &c.). It would therefore appear preferable to measure ζ at the interface glass-aqueous solution. ζ may reliably be determined by the aid of electro-osmosis, or of stream potentials in glass capillaries. But *Haber* and *Klemensiewicz*[2] have demonstrated that there is also a Nernst p.d. at their "glass electrodes." In conjunction with *Rona* I have, therefore, determined, in the first instance, the stream potentials in glass capillaries, and in the second instance the Nernst p.d. at a glass electrode (made, so far as possible, of the same glass) after *Haber* and *Klemensiewicz*.

In measuring the stream potentials we made use of a capillary of an easily-fusible Thüringian glass, 10 cm. long, about $\frac{1}{8}$ mm. in diameter, through which the aqueous solution was forced by the pressure of the nitrogen in a cylinder. The experiments are conveniently and smoothly performed, provided the electrodes be as reversible as possible. Our electrodes were 0·1 N. calomel electrodes; they were joined to the ends of the capillary through tubes charged with a 3 per cent. agar jelly prepared from 0·1 N. solution of KCl. A binant electrometer served for the measurements.

In complete agreement with previous experiences[3] we found the concentration of the electrolytes to be of decisive importance. In concentrations exceeding about 1,000 micromols (millionth parts of a mol) stream potential could no longer be observed; generally concentrations of from 10 to 100 micromols suffice to reduce the ζ of pure water to very small values.

The effect depends essentially upon the kations, their valency and other properties, which we may connect with their adsorbability. Salts with univalent kations such as NaCl, KCl and others are the least effective; salts with bivalent kations, and further also acids, are considerably more effective. With none of these it was, however, possible to reverse the negative charge of the glass into a positive

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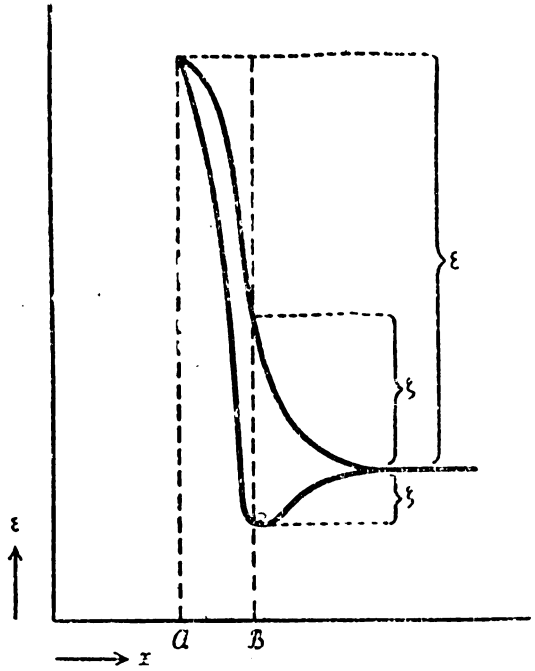
charge. But this reversal is produced by aluminium chloride already at a concentration of 1 or 2 micromols (*i.e.*, about 0·15 mg. per litre), further by crystal violet at about 50 micromols. The reversal with aluminium chloride was also observed when there were present in the solution 150 micromols of KCl in addition to 6 micromols of $AlCl_3$.

The measurements at glass electrodes were carried out exactly as previously by H. and K. A globe of very thin-walled glass dipped into a beaker filled with the electrolyte solution, these solutions being the same as those used for the stream potentials. The glass globe contained 0·1 N. solution of KCl and in it a platinum electrode joined to the binant electrometer. In the beaker was the earthed 0·1 N calomel electrode. Before each series of measurements we repeated the H. and K. sequence of experiments with solutions of $H^{\cdot}$ and OH' ions of various concentrations to make sure of the applicability of the method.

It resulted that we did not find anything, in the experiments after H. and K., of the peculiar effects observed with stream potentials. When the electrolyte solution contained, *e.g.*, 100 micromols of KCl, and we added hydrochloric acid in concentrations increasing from 5 up to 50 micromols, we observed electrometer deflections up to about 50 millivolts, in the sense of increasing acidity. When we took aluminium chloride of the same molar concentration, in the place of HCl, we observed deflections in the same sense attaining 40 millivolts, whilst crystal violet yielded only a small deflection of about 15 millivolts even at a concentration of 200 micromols.

The glass electrode after H. and K. behaves altogether like an $H^{\cdot}$ electrode. Since the $H^{\cdot}$ ion concentration is badly defined in solutions so poor in electrolytes, one cannot well expect to obtain exactly reproducible results. For this reason the same experiments were repeated with buffer mixtures (of sodium acetate and acetic



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acid). The electrometer deflection, observed with a buffer-mixture of a definite $H^{\cdot}$ ion concentration, was not in the slightest way changed by the addition of aluminium chloride and of crystal violet in concentrations up to 100 micromols. It follows from these experiments that ζ and ϵ are certainly not identical. We must, on the contrary, assume that there is a space charge at the solid interface, a diffuse double layer (after *Gouy*[4]) which projects rather deeply into the liquid. ζ represents the part of the double layer which lies entirely in the liquid, that is to say, the p.d. between the liquid film adhering to the wall and the movable liquid. On the other hand, ϵ is the p.d. between the acid wall itself and the interior of the liquid. The annexed diagram illustrates the relation. The ordinates represent the potentials, the abscissæ the distances from the solid wall, measured in the liquid. The fixed wall is on the left of A; between A and B is the film of liquid adhering to the wall; to the right of B the movable liquid. The diagram shows that with the possible variations of the potential curve, ζ may even differ from ϵ in sign.

Since ζ lies entirely within the liquid we have according to *Pellat* and *Perrin*[5], and in distinction from *Helmholtz*, to take the dielectric constant into consideration. When we then calculate the p.d. ζ after the formula of *Helmholtz*, $\zeta = 4\ \pi\eta\lambda\ \mathrm{E/p.D.}$[6], we find values up to about 100 millivolts, smaller therefore than the ϵ values, as we should indeed expect on our assumption. The potential ϵ being, in the experiments of H. and K., quite independent of ions such as those of aluminium and crystal violet, we understand why nobody, in taking p.d. measurements after Nernst at metallic electrodes has ever noticed any influence of the valency and adsorbability of such foreign ions, whilst that influence completely dominates the phenomena of electro-kinetic processes.

When we attempt to explain the influence of electrolytes upon the p.d. ζ, we have to bear in mind that according to *Gouy*[7] the thickness of the film projecting into the liquid decreases strongly as the concentration of the electrolyte increases. With higher concentrations the film soon becomes so thin and penetrates to so small a depth into the liquid that we can, in electrokinetic experiments, no longer separate the two coatings from one another. This point and the increasing conductivity of the solution account for the vanishing of the electrokinetic effect at higher electrolytic concentrations. With respect to the influence of the nature of the ions we seem to be constrained to ascribe importance to the adsorbability and to the valency essentially in connection with the adsorbability.[8] It is noteworthy that we meet with this striking effect of the aluminium ion and of other ions of high valency not only in electrokinetic experiments at glass walls, but also at phase boundaries of entirely different nature. We find it, to quote a few examples, in the kataphoresis of little droplets of hydrocarbons[9] and of air bubbles,[10] further in the coagulation—which, we know, is intimately connected with electrokinetic processes—of arsenic trisulphide,[11] and of gold[12] and silver sols,[13] &c. The facts suggest that we have in all these cases to deal with a distribution of the ions, depending upon the nature of the ions, in the layers of water directly adhering to the different phases.

There are, moreover, also electrochemical phenomena in which both ϵ and ζ come into play. Such are the capillary-electric phenomena at the interface mercury-aqueous solutions. The limiting surface tension of mercury is certainly not merely to be interpreted as a function of the potential difference and thus of the mercuric ions

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which determine the p.d. The distribution of the ions in the water-film adjacent to the mercury surface will certainly influence the surface tension.[14] When now we have ions present of pronounced adsorbability and consequently deal with a characteristic ζ, the maximum surface tension will not be attained at the same potential as in the presence of capillarily-active electrolytes; we thus find a displacement of the maximum of surface tension. It is in accord with this view that the maximum of capillarily-active ions of opposite charges is displaced also in the opposite direction.[15] Experiments made by myself and Miss *Wreschner*, Ph.D., show that basic and acid dyes which are so effective in electrokinetic phenomena, are prominent also in this respect. Kations of basic colouring matters, like other kations which are capillarily-active, displace the maximum towards the ascending positive branch of the curve of electrocapillarity; anions of acid dyes, like other capillarily-active anions, shift the maximum over to the descending negative branch. This displacement will also be noticeable at higher electrolytic concentrations, at which ζ has only small values; for the effect of the potential gradient lying in the liquid may still be very marked, although we measure only small potential differences in electrokinetic experiments owing to the high conductivity concerned. That the maximum of such capillarily-active ions is not only displaced, but actually lowered, accords with the fact that capillarily-active substances may lower any interfacial tension.[16] In electrolytes, the anions and kations of which are both particularly inactive as regards capillarity, the p.d. is zero for the maximum of surface tension. This condition occurs for mercury in a solution of KNO_3; in this instance the electrocapillary curve deviates merely by a few tenths of one per cent. from the parabolic shape—in accordance with the *Lippmann-Helmholtz* theory.[17]

Looking back, we may answer the question raised in the introduction in the sense that the *Nernst* potential difference ϵ is by no means identical with the electrokinetic p.d. ζ. The *Nernst* potential ϵ represents the total difference between the interior of the first phase and that of the second phase; the electrokinetic potential ζ represents that portion of the difference which falls within the displaceable liquid layers.

[1] *Gesammelte Abhandl.*, I., p. 855.
[2] *Zeitschr. Physik. Chem.*, **67**, 385 (1909).
[3] Krüyt, *Kolloid Zeitschr.*, **22**, 81 (1918); also v. Elissafoff, *Zeitschr. Physik. Chem.*, **79**, 385 (1912), "Electro-osmosis in Glass Capillaries."
[4] *Journ. de Phys.*, **9**, 457 (1910).
[5] *Journ. de Chim. Phys.*, **2**, 601 (1904)
[6] p = excess pressure forcing the liquid through a capillary in a Poiseuille stream; E = p.d. between the electrodes; η = viscosity of the liquid; D = dielectric constant; λ = specific conductivity.
[7] *Loc. cit.*, p. 5.
[8] Freundlich, *Kapillarchemie*, pp. 243, &c. (1909).
[9] Powis, *Zeitschr. Physik. Chem.*, **89**, 91 (1915).
[10] McTaggart, *Phil. Mag.*, [6], **27**, 297 (1914).
[11] Freundlich, *Zeitschr. Physik. Chem.*, **44**, 129 (1903).
[12] v. Elissafoff, *loc. cit.*, p. 2.
[13] Burton, *Phil. Mag.*, [6], **12**, 472 (1906).
[14] Gouy, *Ann. d. Chim. et d. Phys.* [7], **29**, 145 (1903); [8], 3, 291 (1906); [8], 9, 75 (1906). Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).
[15] Gouy, *loc. cit.*, note 6, p. 8.
[16] Freundlich, *Kapillarchemie*, pp. 187, &c. (1909).
[17] Krüger, *Zeitschr. Elektrochem.*, **19**, 617 (1913).

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DISCUSSION

Prof. J. W. McBain: It is an almost necessary corollary to the theory of colloidal electrolytes that electrical endosmosis is due entirely to the free ions of the double layer, that is, that the charges involved are due to the adsorption of one ion which is thereby fixed upon the surface, leaving its partner as an ordinary ion, somewhere in the neighbourhood, but free to move in an electric field, carrying its water of hydration with it, and possibly also the solution itself through friction or viscous drag.

Mr. Darke has been carrying out some measurements in the Bristol laboratory to test this explanation of electrical endosmosis. Although I can only refer to preliminary results which must be accepted with all due reserve, pending the use of improved apparatus, nevertheless, these preliminary results are sufficiently striking to be referred to here.

Mr. Darke finds, first, that the conductivity of a solution of potassium chloride is about 9 per cent. greater when measured in coarse capillary tubes of fused silica of about $\frac{1}{4}$ mm. diameter, than when it is measured in bulk in the open. This extra 9 per cent. of conductivity is, according to our view, to be ascribed to the extra potassium ions, equivalent to the chlorine ions which have been adsorbed; that is, we have the conductivity corresponding to the average bulk concentration of the potassium chloride, superadded to which comes the conductivity due to the excess of the potassium ions. This increase is only observed after repeated rinsing with fresh solution; the effect initially observed is, of course, in the opposite direction.

A second interesting result follows from these observations when we calculate the amount of chlorine ions which have been adsorbed upon the surface of the silica. Assuming a density of 2 for the surface film, which is the density of solid potassium chloride where the potassium and chlorine ions in the space lattice are equally responsible for the volume and density, we find that the amount of chlorine ion equivalent to the excess of free potassium ions, as deduced from the conductivity experiments, is just sufficient to cover the surface of the fused silica with a layer of chlorine ion one molecule deep.

Our next step has been to attempt some approximate absolute measurements of electric endosmosis for, as far as I know, none such exist. Mr. Darke has as yet only a few rough and highly-approximate measurements with provisional apparatus, but it has interested us very greatly to find that the amount of electric endosmosis which is observed, taken in conjunction with the results of the conductivity measurements, might indicate that potassium ion is hydrated in $\frac{N}{50}$ solution to the extent of about a dozen molecules of water on each ion of potassium. This is just about the degree of hydration which is required to correct the existing classical dissociation theory into a quantitative hydrate form of that theory, which is desirable in order to remove some of its outstanding difficulties such as, for example, the apparent deviations of electrolytes from the mass law.

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Mr. A. S. E. Ackermann wrote that for the last three years he had been engaged on an investigation into the physical properties of London clay, which, owing to its being taken from just below the surface soil, was of yellow colour. One particularly interesting result which the experiments had brought out was the phenomenon which he has called the pressure of fluidity, which was got out by the following experiment.

A vertical guide and load-rod, with the equivalent of a ball and socket joint at its upper end, had fixed to its lower end, rigidly and at right angles to the rod, various-sized duralumin discs, one at a time. The disc was placed on the surface of well-puddled clay in a container, the clay containing a known percentage of water. Loads were applied to the top end of the guide-rod, and owing to the ball and socket arrangement the resultant of these loads was co-axial with the axis of the guide-rod. Measurements of the penetration produced by each increment of load were taken, and each load was allowed to act for 10 minutes before the measurement of penetration was recorded and a fresh increment of load added. The curves of these experiments (each dealing with either a different-sized disc or the same disc in clay containing a different percentage of water) were plotted, with the loads as ordinates and penetrations as abscissæ, and are roughly the quadrant of a circle, and then when a certain stress is reached the clay seems suddenly to break down, and the penetration continues apparently indefinitely at a constant speed without additional load until the disc is stopped from further motion by the bottom of the container. Roughly, during the early part of each experiment, the speed of penetration is about 1 mm. per minute; when the pressure of fluidity is reached, the speed becomes 1 cm. per minute. On making three experiments, in particular, with clay containing 29 per cent. of water, and using discs 26 mm., 37 mm. and 63 mm. in diameter, the same phenomenon was discovered in each case, and when the loads were divided by the areas of the respective discs the mean stress under the disc was 597 grms. per sq. cm.

Mr. Ackermann stated that he had never failed to obtain the pressure of fluidity, except in one case, where the clay contained only 17·5 per cent. of water, and was then so hard that, in spite of the stress being 11,540 grms. sq. cm. (= 10·5 tons/sq. foot), the penetration of the disc was only 5 mms., and there was no means of further increasing the stress. Two other experimenters have since repeated the experiment, and found the same effect in the same conditions. These are P. M. Crosthwaite, who also used London clay, and Lt.-Col. H. R. Lordly, who used some yellow clay obtained in Ithaca, New York, U.S.A.

As far as the experiments have gone, it has been found that the pressure of fluidity increases very rapidly as the water content decreases. If the experiments be plotted with the pressure of fluidity in kilos per sq. cm. as ordinates, and the percentage of water in the clay as abscissae, then the drier end of the curve (that is, for clays containing between 25½ per cent. and 22 per cent. of water) is a straight line, the equation to which is $p' = 39{\cdot}5 - 1{\cdot}48\ w'$, where p' is the intensity of pressure under the disc in kilos per sq. cm. and w' is the percentage of water content. Between 25½ per cent. and 38 per cent. of water, the experimental results agree more closely with the curve, the equation to which is $p' = \frac{1{,}073 \times 10^{10}}{(w')^7}$

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It is considered that this pressure of fluidity is of importance in connection with land slides (where there is a low-lying layer of clay), cuttings, foundations of all kinds, retaining walls, piles and that it is probably closely associated with the viscosity of the clay when it is thus acting like a fluid. The experiments have shown that a general pressure on the *whole* mass of clay does *not* render it fluid-like; only when a portion is loaded does the phenomenon occur.

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APPENDIX I

THE PROTEINS AND COLLOID CHEMISTRY*

BY

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I

The proteins, like certain other constituents of protoplasm, are colloidal in character, *i.e.* they are not able to diffuse through animal membranes which are permeable to crystalloids. For this reason a number of authors have tried to explain the behaviour of proteins from the view-point of the newer concepts of colloid chemistry. Foremost among these concepts is the idea that the reactions between colloids and other bodies are not determined by the purely chemical forces of primary or secondary valency, but follow the rules of "adsorption." Although a number of authors, during the last 20 years, *e.g.*, Bugarszky and Liebermann, Hardy, Pauli, Robertson, Sörensen, and others, have advocated a chemical conception of the reactions of proteins, their experiments failed to convince the other side, since these experiments could just as well be explained on the basis of the adsorption theory. There were two reasons for this failure. First, the experiments did not show that ions combined with proteins in the typical ratio in which the same ions combine with crystalloids. This proof only became possible when it was recognised that the hydrogen ion concentration of the protein solution determines the amount of ion entering into combination with a protein, and that therefore the ratios in which different ions combine with proteins must be compared for the same hydrogen ion concentrations. Since the former workers were in the habit of comparing the effects of the same quantities of acid or alkali added instead of comparing the behaviour of proteins at the same hydrogen ion concentration, they were not able to furnish the final proof for the purely chemical character of the combinations between ions and proteins, and nothing prevented chemists from assuming that proteins formed only adsorption compounds with acids, bases and neutral salts.

The second reason for the failure to prove the purely chemical character of the protein compounds lay in the so-called Hofmeister series of ion effects. Hofmeister was the first to investigate the effects of different salts on the physical properties of proteins, and he and his followers observed that the relative effect of anions on the precipitation, the swelling and other properties of proteins was

* The writer's experiments, on which this address is based, have appeared in the *J. Gen. Physiol.*, 1918-19, i, 39, 237 363, 483, 559; 1919-20, ii, 87; 1920-21, iii, 85, 247. 391.

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very definite, and that the anions could be arranged in definite series according to their relative efficiency, the order being independent of the nature of the cation. Similar series were also found for the cations, though these series seemed to be less definite. These Hofmeister series were a puzzle, inasmuch as it was impossible to discover in them any relation to the typical combining ratios of the ions, and this lack of chemical character in the Hofmeister series induced chemists to explain these series on the assumption of a selective adsorption of these ions by the colloids.

To illustrate this, we will quote the order which, according to Pauli, represents the relative efficiency of different acids on the viscosity of blood albumin—

HCl > monochloracetic > oxalic > dichloracetic > citric > acetic > sulfuric > trichloracetic acid,

where HCl increased the viscosity most and trichloracetic or sulfuric least. In this series the strong monobasic acid HCl is followed by the weak monochloracetic acid, this is followed by the dibasic oxalic acid; later follows a weak tribasic citric acid, then the very weak monobasic acetic acid, then the strong dibasic sulfuric acid, and finally again a monobasic acid, trichloracetic. Pauli is a believer in the chemical theory of the behaviour of proteins, but it is impossible to harmonize his series of anions with any purely chemical theory of the behaviour of proteins.

The ion series of Hofmeister are no more favourable for a chemical conception. Thus, according to Hofmeister, gelatin swells more in chlorides, bromides and nitrates than in water, while in acetates, tartrates, citrates or sugar it swells less than in water. R. Lillie arranges ions according to their depressing effect on the osmotic pressure of gelatin solution in the following way—

$$Cl > SO_4 > NO_3 > Br > I > CNS.$$

These series again betray no relation to the stoichiometrical properties of the ions. As long as these Hofmeister ion series were believed to have a real existence it seemed futile to decide for or against a purely chemical theory of the behaviour of proteins since even with a bias in favour of a chemical theory the ion series remained a puzzle.

The writer believes to have removed these difficulties by using protein solutions of the same hydrogen ion concentration as the standard of comparison. In this way he was able to show that acids, alkalies and neutral salts combine with proteins by the same chemical forces of primary valency by which they combine with crystalloids, and that, moreover, the influence of the different ions upon the physical properties of proteins can be predicted from the general combining ratios of these ions. The so-called Hofmeister series have no real existence, being the result of the fact that the older workers failed to measure the most important variable in the case, namely, the hydrogen ion concentration of their protein solutions, a failure for which they cannot be blamed since the methods were not sufficiently developed.

II

Pauli and a number of other workers assume that both ions of a neutral salt are adsorbed simultaneously by non-ionised protein molecules. If we consider the hydrogen ion concentration of the proteins we can show that only the cation or only the anion or that

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neither ion can combine at one time with a protein; and that it depends solely on the hydrogen ion concentration of the solution which of the three possibilities exists.

Proteins exist in three states, defined by their hydrogen ion concentration, namely: (*a*) as non-ionogenic or isoelectric protein, (*b*) as metal proteinate (*e.g.*, Na or Ca proteinate), and (*c*) as protein-acid salts (*e.g.*, protein chloride, protein sulfate, &c.). We will use gelatin as an illustration. At one definite hydrogen ion concentration, namely, $10^{-4.7}$ N (or in Sörensen's logarithmic symbol at $p\mathrm{H} = 4{\cdot}7$), gelatin can combine practically with neither anion nor cation of an electrolyte. At a $p\mathrm{H} > 4{\cdot}7$ it can combine only with cations (forming metal gelatinate, *e.g.* Na gelatinate), at a $p\mathrm{H} < 4{\cdot}7$ it combines with anions (forming gelatin chloride, &c.). This was proved in the following way:—Doses of 1 gm. of finely powdered commercial gelatin (going through sieve 60, but not through 80), which happened to have a $p\mathrm{H}$ of 7·0, were brought to a different hydrogen ion concentration by putting them for 1 hour at about 15° C. into 100 c.c. of HNO_3 solutions varying in concentration from M/8192 to M/8. After this they were put on a filter, the acid being allowed to drain off, and were washed once or twice with 25 cc. of cold water (of 5° C. or less) to remove remnants of the acid between the granules of the powdered gelatin. These different doses of 1 gm. of gelatin, now possessing a different $p\mathrm{H}$, were all put for 1 hour into beakers containing the same concentration, *e.g.* M/64, of silver nitrate at a temperature of 15° C. They were then put on a filter and washed six or eight times each with 25 c.c. of ice-cold water; the wash water must be cold, since otherwise the particles will coalesce and the washing will be incomplete. This washing serves the purpose of removing the $AgNO_3$ held in solution between the granules, thus allowing us to ascertain where the Ag is in combination with gelatin and where it is not in combination, since the Ag not in combination with gelatin can be removed by the washing while the former cannot (or at least only extremely slowly by altering the $p\mathrm{H}$). After having removed the $AgNO_3$ not in combination with gelatin by washing with ice-cold water, we melt the gelatin by heating to 40° C., adding enough distilled water to bring the volume of each gelatin solution to 100 c.c., determine the $p\mathrm{H}$ of each solution potentiometrically or colorimetrically, and expose the solutions in test-tubes to light, the previous manipulations having been carried out in a dark room (with the exception of the determination of $p\mathrm{H}$, for which only part of the gelatin solution was used). In 20 minutes all the gelatin solutions with a $p\mathrm{H} > 4{\cdot}7$, *i.e.* from $p\mathrm{H}$ 4·8 and above, become opaque and then black, while all the solutions of $p\mathrm{H} < 4{\cdot}7$, *i.e.* from 4·6 and below, remain transparent even when exposed to light for months or years. The solutions of $p\mathrm{H}$ 4·7 become opaque, but remain white, no matter how long they may have been exposed to light. At this $p\mathrm{H}$—the isoelectric point—gelatin is not in combination with Ag, but it is insoluble. Hence the cation Ag is only in chemical combination with gelatin when the $p\mathrm{H}$ is $>4{\cdot}7$. At $p\mathrm{H}$ 4·7 or below gelatin is not able to combine with Ag ionogenically. This statement was confirmed by volumetric analysis.

The same tests can be made for any other cation the presence of which can be easily demonstrated. Thus when powdered gelatin of different $p\mathrm{H}$ is treated with $NiCl_3$ and the $NiCl_3$ not in combination with gelatin be removed by washin g with ice-cold water, the presence of Ni can be demonstrated in all gelatin solutions with a $p\mathrm{H} > 4{\cdot}7$

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by using dimethylglyoxime as an indicator. All gelatin solutions of *p*H of 4·8 or above assume a crimson colour upon the addition of dimethylglyoxime, while all the others remain colorless. When we treat gelatin with copper acetate, and wash afterwards, the gelatin is blue and opaque when its *p*H is 4·8 or above, but is colorless and clear for *p*H$<$4·7. Most striking are the results with basic dyes, *e.g.*, basic fuchsin or neutral red, after sufficient washing with cold water; only those gelatin solutions are red whose *p*H is above 4·7, while the others are colorless.

On the acid side of the isoelectric point, *i.e.* at *p*H$<$4·7, the gelatin is in combination with the anion of the salt used. This can be demonstrated in the same way by bringing different doses of powdered gelatin to different *p*H and treating them for 1 hour with a weak solution of a salt whose anion easily betrays itself, *e.g.* M/128 $K_4Fe(CN)_6$. If, after this treatment, the powdered gelatin is washed six times with cold water to remove the $Fe(CN)_6$ not in chemical combination with gelatin, and if 1 per cent. solutions of these different samples of gelatin are made, it is found that when the *p*H is $<$4·7 the gelatin solution turns blue after a few days (due to the formation of ferric salt), while solutions of gelatin with a *p*H of 4·7 or above remain permanently colorless. Hence gelatin enters into chemical combination with the anion $Fe(CN)_6$ only when the *p*H is $<$4·7. The same can be demonstrated through the addition of ferric salt when gelatin has been treated with NaCNS, the anion CNS being in combination with gelatin only where the *p*H is $<$4·7. Acid dyes, like acid fuchsin, combine with gelatin only when the *p*H is $<$4·7.

In this way it can be shown that when the *p*H is $>$4·7 gelatin can combine only with cations; when the *p*H is $<$4·7 it can combine only with anions, while at *p*H 4·7 (the isoelectric point) it can combine with neither anion nor cation. The idea that both ions influence a protein simultaneously is no longer tenable.

It follows also that a protein solution is not adequately defined by its concentration of protein, but that the hydrogen ion concentration must also be known since each protein occurs in three different forms—possibly isomers—according to its hydrogen ion concentration.

In the experiments just discussed it was necessary to wash the powdered gelatin to find out at which *p*H an ion was in combination with the gelatin. This has led some authors to the belief that in all my experiments the washing was a necessary part of the procedure. I therefore will call especial attention to the fact that the experiments to be described in the rest of the paper were carried out with isoelectric gelatin to which just enough acid or alkali was added to bring it to the hydrogen ion concentration required for the purpose of the experiment.

III

When a protein is in a salt solution, *e.g.* NaCl, it will combine with Na forming sodium proteinate as soon as the *p*H is higher than the isoelectric point of the protein; when, however, the *p*H falls below that of the isoelectric point of the protein the Na is given off and protein chloride is formed.

Moreover, the writer has been able to show by volumetric analysis that the quantity of anion or cation in combination with the protein is an unequivocal function of the *p*H. When we add HCl to isoelectric gelatin and determine the *p*H we always find the same amount of Cl

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in combination with a given mass of originally isoelectric gelatin for the same *p*H; so that if we know the *p*H and the concentration of originally isoelectric gelatin present, we can also tell how much Cl is in combination with the protein for this *p*H. The same is true when we add an alkali to the isoelectric gelatin. For the same *p*H the amount of cation in combination is always the same. These facts have led the writer to propose the following theory:—When we add an acid, *e.g.* HCl, to isoelectric gelatin (or any other isoelectric protein) an equilibrium is established between free HCl, protein chloride, and non-ionogenic or isoelectric protein, and when we add an alkali an equilibrium is established between metal proteinate, non-ionogenic or isoelectric protein, and the hydrogen ion concentration. Sörensen was led to a similar view on the basis of entirely different experiments.

IV

This fact that the hydrogen ion concentration of a protein solution determines the quantity of protein salt formed is the basis on which

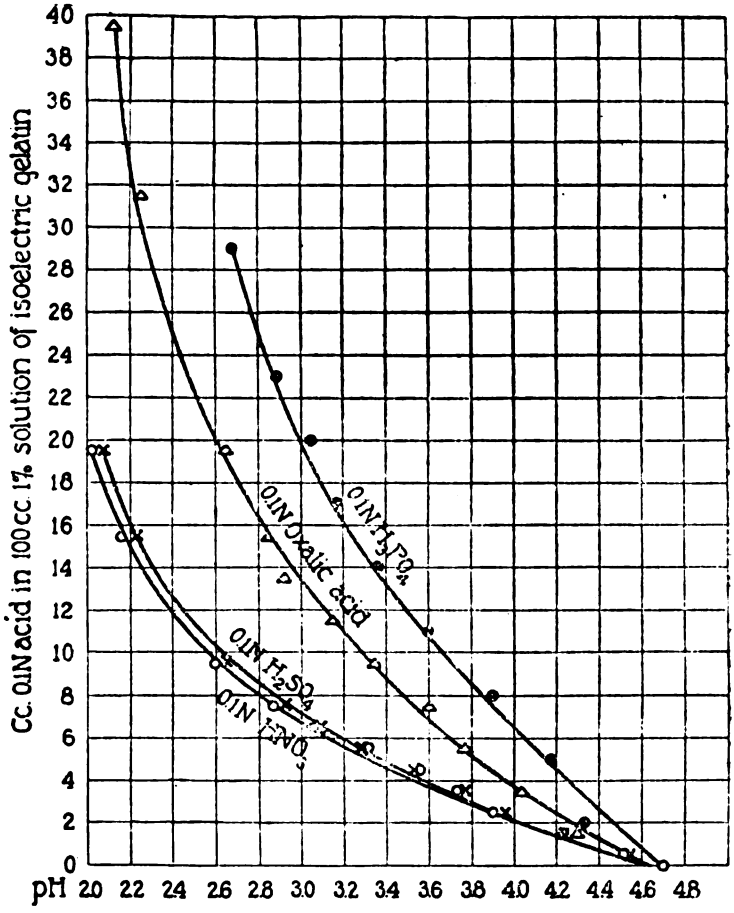

Fig. 1.—The ordinates represent the c.c. of 0·1 N acid in 100 c.c. of 1 per cent. solution of isoelectric gelatin required to bring the solution to the *p*H indicated in the abscissæ. The curves for 0·1 N, H_2SO_4 and 0·1 N, HNO_3 are identical, while the values for H_3PO_4 and oxalic acid differ, being approximately in the ratio of HNO_3 : oxalic acid : H_3PO_4 as 1 : 2 : 3.

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the following proof for the purely chemical character of the combination between proteins and other bodies rests. The experiments mentioned thus far in this paper do not yet allow us to decide whether the ions are "adsorbed" or in chemical combination with the proteins. We will now show that acids and bases combine with proteins in the same way as they combine with crystalline compounds, namely, by the purely chemical forces of primary valency. The combination between acids and proteins is analogous to that between acids and NH_3, and the combination between bases and proteins is analogous to that between CH_3COOH and an alkali. This can be proved in the following way:—We know that a weak dibasic or tribasic acid gives off one hydrogen ion more readily than both or all three; while in a strong dibasic acid, like H_2SO_4, both hydrogen ions are held with a sufficiently small electrostatic force to be easily removed. If the forces which determine the reaction between these acids and proteins are purely chemical it would follow that three times as many c.c. of 0·1 N, H_3PO_4 are required to bring 100 c.c. of 1 per cent. solution of isoelectric gelatin to a given *p*H, *e.g.* 3·0, as are required in the case of HNO_3 or HCl; while twice as many c.c. of 0·1 N oxalic as of HNO_3 should be required. On the other hand, it should require just as many c.c. of 0·1 N, H_2SO_4as HNO_3. Fig. 1 shows that this is the case. The ordinates of this figure are the c.c. of 0·1 N acid required to bring 1 gm. of isoelectric gelatin to the *p*H indicated in the abscissæ by the four acids mentioned, namely, HNO_3, H_2SO_4, oxalic and phosphoric acids. The curves for H_2SO_4 and HNO_3 are identical, while, for the same *p*H, the value for H_3PO_4 is always approximately three times, and the value for oxalic acid is always approximately twice as high as for HNO_3.

On the basis of the same reasoning as applied to acids we should expect that equal numbers of c.c. of 0·1 N, $Ca(OH)_2$ and $Ba(OH)_2$ as of LiOH, NaOH and KOH should be required to bring 100 c.c. of a 1 per cent. solution of isoelectric gelatin to the same *p*H, and the writer was able to show that this is the case. Similar results were obtained with crystalline egg albumin.

When we have a solution of a gelatin-acid salt of originally 1 per cent. isoelectric gelatin and of a certain *p*H, *e.g.* 3·0, we have free acid in the solution and a certain amount of the anion of the acid in combination with gelatin. We can find out by volumetric analysis how much of the anion is in combination with the protein by making certain corrections discussed in former papers. In this way it can also be ascertained that all weak dibasic acids combine in molecular proportions with isoelectric protein, while strong dibasic acids and diacidic alkalies combine in equivalent proportions with proteins, as is shown by Table I. It follows from this table that for the same *p*H the amount of HNO_3, oxalic and phosphoric acids in combination with the same quantity of originally isoelectric gelatin is always in the proportion of 1 : 2 : 3.

TABLE I

C.c. of 0·01 *N acid in combination with* 10 *c.c. of a* 1 *per cent. gelatin solution at different p*H.

*p*H.	3·1	3·2	3·3	3·4	3·5	3·7	3·9	4·1	4·2	4·3
HNO_3 -	4·35	4·1	3·6	3·2	2·85	2·45	1·9	1·45		0·75
Oxalic acid -	9·6	8·75	7·6	6·7	6·00	4·3	3·0		1·65	
H_3PO_4 -		12·4	10·4	9·8	9·00	7·4	5·8	4·5	2·6	2·1

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We can, therefore, state that the ratios in which ions combine with proteins are identical with the ratios in which the same ions combine with crystalloids. Or, in other words, the forces by which gelatin and egg albumin (and probably proteins in general) combine with acids or alkalies are the purely chemical forces of primary valency.

V

The most important fact for our purpose is that from the combining ratios just mentioned the influence of acids and bases on the physical properties of proteins can be predicted. This influence is altogether different from that stated in the so-called Hofmeister series of ions or by the ion series of Pauli and his collaborators, and this difference is due to the fact that these latter authors compared the effects of equal quantities of acids or alkalies while we found it necessary to compare the physical properties of solutions of proteins of the same hydrogen ion concentration. If this is done the following rule is found :—All those acids whose anion combines as a monovalent ion raise the osmotic pressure, viscosity, swelling of protein about twice as much as the acids whose anion combines as a bivalent anion for the same *p*H. The same valency rule holds also for the cations of different alkalies.

We have seen that at the same *p*H three times as many c.c. of

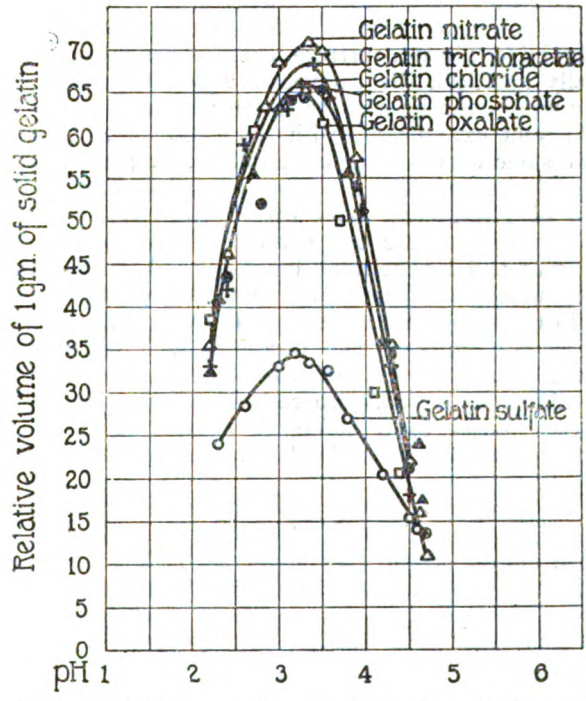

Fig. 2.—Influence of different acids upon the swelling of gelatin when plotted over *p*H as abscissæ. The curves show that nitric, trichloracetic, hydrochloric, phosphoric, oxalic and citric acids cause approximately the same degree of swelling, while sulfuric acid causes only about one-half the amount of swelling. In the case of gelatin sulfate the anion is divalent; in the case of the other acids used it is monovalent. According to the Hofmeister series the curves for phosphate, oxalate and citrate should coincide with that of sulfate, instead of coinciding with that of chloride.

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0·1 N, H_3PO_4 as of HNO_3 are in combination with 1 gm. of originally isoelectric gelatin in 100 cc. of solution. If follows from this that the anion of gelatin phosphate is the monovalent ion H_2PO_4 and not the trivalent anion PO_4. It follows likewise from the combining ratios discussed that the anion of oxalic acid in combination with protein is the monovalent anion HC_2O_4. The same is true for all weak dibasic or tribasic acids, namely, that they combine with proteins forming protein salts with monovalent anion. It follows also from the combining ratios that the salt of a protein with a strong dibasic acid, as H_2SO_4, however, must have a divalent anion, *e.g.* SO_4. If we compare the viscosity or osmotic pressure of 1 per cent. solutions of originally isoelectric gelatin with different acids of the same *p*H, we find that these properties are identical for all gelatin salts with monovalent anion; in other words, 1 per cent. solutions of gelatin chloride, bromide, nitrate, tartrate, succinate, citrate or phosphate have all the same viscosity, and the same osmotic pressure at the same *p*H. The same is true for the swelling (Fig. 2). If we plot the curves for these three properties with *p*H as abscissæ and the values for osmotic pressure, viscosity and swelling as ordinates, we get practically identical curves for gelatin chloride, bromide, nitrate, tartrate, succinate, citrate and phosphate. The values for swelling are a minimum at *p*H 4·7 (the isoelectric point of gelatin), they rise rapidly with the fall of *p*H until they reach a maximum at *p*H about 3·2, and then they drop again. Each curve is the expression of an individual experiment. The maximum in the curves for gelatin chloride, bromide, nitrate, tartrate, succinate, citrate, and phosphate is practically identical, the variations between the values for these acids lying within the limit of variation which we may expect if we plot six different experiments with the same acid. When, however, we plot the same curves for gelatin sulfate, we get curves which are considerably lower, reaching a height of only one-half (or a little less) than those of gelatin-acid salts with monovalent anions. It may be of interest to compare our curves with those expected on the basis of Pauli's and Hofmeister's ion series. According to the latter theory the curves for phosphates, oxalates, citrates and tartrates should be in the region of the SO_4 curve, but not in the region of the Cl curve. Those authors who observed such differences did not measure the hydrogen ion concentration, attributing the effects due to the difference in the hydrogen ion concentration of their gelatin solutions erroneously to a difference in the anion effect. These elementary errors form the basis of a number of speculations current in biology and pathology.

When we compare monobasic acids of different strength, *e.g.* acetic, mono-, di-, and trichloracetic acids, we find that the weaker the acid the more acid must be contained in a 1 per cent. solution of originally isoelectric gelatin to bring it to the same *p*H. If we compare the effect of these four acids on the osmotic pressure of gelatin we find that it is (within the limits of accuracy of these experiments) identical for the same *p*H. The curves for the influence of these four acids on the osmotic pressure of gelatin solution are practically identical when plotted over the *p*H as abscissæ; and, moreover, the curves are identical with the curves for HCl or H_3PO_4 in Fig. 1. The explanation of this fact is that at the same *p*H the same mass of originally isoelectric gelatin is in combination with the same quantity of these four acids, and since the anions of these four acids are all monovalent the curves must be identical.

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As far as the alkalies are concerned, we notice that the curve representing the effect of the weak base NH_4OH on the physical properites of proteins is the same as that for the strong bases LiOH, NaOH, KOH when plotted over *p*H as abscissæ, while the curves representing the effect of $Ca(OH)_2$ or $Ba(OH)_2$ on the same properties are considerably lower.

It is obvious that the valency of the ion in combination with the protein has a noticeable influence on the properties of the protein salt formed, while the protein salts with ions of the same valency have all the same properties. The fact of the greatest importance is, however, that the influence of acids and bases on the physical properties of proteins is the expression of the combining ratios of the acids or bases with proteins so that we are able to predict the value of these physical properties from the combining ratios. This fact seems to give a final decision in favour of a purely chemical theory of these influences and against the colloidal theories as based on the Hofmeister or Pauli ion series.

The behaviour of the proteins therefore contradicts the idea that the chemistry of colloids differs from the chemistry of crystalloids.

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APPENDIX II

ON THE INTERNAL PRESSURE OF LIQUIDS

BY

H. KNEEBONE TOMPKINS, D.Sc.

This paper was written in 1896 as an Inaugural Dissertation for the Degree of Doctor of Science of the University of London. As it has never been published, the Joint Committee which organised the General Discussion is of opinion that the present Report affords a suitable opportunity for publishing the results of an investigation of historical importance by a very early and accurate worker in the field of colloidal physics.

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ON THE INTERNAL PRESSURE OF LIQUIDS

BY

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MANY attempts have been made to determine osmotic pressures and rates of diffusion by means of colloidal septa, but the results have generally been very complex, partly on account of the change of molecular aggregation which takes place with change of concentration in aqueous solutions, and partly because swollen colloids are rarely perfectly impervious to the diffusing substances. No examination, so far as I am aware, has been made of the expansion of the colloid itself when placed in a liquid in which it can swell, or of any change of volume which the swollen colloid may experience when submitted to the action of saline solutions. It seemed to me probable that the swelling of colloids might be due to osmotic pressure, and that in the swollen colloid we might have a substance sensitive to such pressures.

For the purpose of the investigation the ordinary colloids such as gelatin, agar-agar, &c., which swell in water, were discarded owing to the above-mentioned complexity, and use was made of a peculiar property of indiarubber.

If pure caoutchouc be placed in carbon bisulphide it swells up considerably and eventually dissolves, forming a thick viscous liquid. Vulcanised indiarubber, on the other hand, behaves quite differently. It swells rapidly at first, afterwards more and more slowly, but preserves its original form, and after about five hours reaches its maximum volume, which in the case of black rubber-tubing is six to seven times that which it originally possessed. The matter extracted by the carbon bisulphide consists mainly of uncombined sulphur, the amount of rubber dissolved being not greater than one per cent. of the substance taken. The indiarubber in its expanded state preserves a good deal of its original elasticity, and if exposed to the air gradually contracts to its original volume and is to all appearance completely unaltered. It seemed probable that the expanded rubber would be sensitive to the osmotic pressure of substances added to the carbon bisulphide, and this has proved to be the case.

The proposed method of experiment consisted in placing a piece of vulcanised rubber in carbon bisulphide until it had reached its maximum volume, which was to be determined by some suitable means, and then dissolving in the carbon bisulphide a given proportion of some other substance and noting any further increase or decrease of volume.

General Properties of Indiarubber.—The material used for these experiments was ordinary black indiarubber tubing of ¼ inch external diameter. It was cut into lengths of one inch and was extracted two or three times with carbon bisulphide in order to remove uncombined sulphur, as it was thought that the latter might influence the results by its osmotic pressure. The rubber was then exposed to the air until thoroughly free from carbon bisulphide.

Specific Gravity.—This value is very constant for the same sample of tubing. The following are six determinations taken at random :—

1 grm. of rubber = 1·0638 c.c.
1·0640
1·0684
1·0655
1·0623
1·0689

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Maximum Expansion of Rubber in Carbon Bisulphide.—A weighed piece of indiarubber tubing was placed in carbon bisulphide until thoroughly expanded. It was then hooked out on a piece of bent wire, and quickly dropped into a weighing-tube which had been lined with filter-paper. The stopper was at once inserted, and the tube rolled round in order to remove carbon bisulphide adhering to the rubber. The tube was then opened for a moment and the paper removed with the balance-tongs. The whole was then weighed. From the increase in weight of the rubber the volume of the absorbed carbon bisulphide can be calculated, if the specific gravity of the latter at the temperature of the experiment is known; and this volume added to the volume of the piece of rubber taken will give the total volume of the rubber when expanded, on the assumption that the volume of the expanded rubber is made up of the volume of the original rubber and that of the absorbed carbon bisulphide (Method B).

As a check to this result the weighing-tube was next opened and filled up with recently boiled water (if ordinary water is used the rubber soon becomes coated with air-bells), the stopper carefully inserted, and the whole weighed. In this way a direct determination of the volume of the expanded rubber is effected (Method A). The weighing-bottle had a well-fitting stopper in which a groove was filed to allow the excess of water to escape, and it was always inserted in the same position and with approximately the same pressure. The bottle was carefully calibrated, and it was found that consecutive weighings when full of water did not differ by more than ·005 grm. The pieces of rubber taken weighed about ·7 grm. The following results were obtained:—

Maximum Volume calculated on 1 c.c. of Rubber

	Method A.	Method B.
Piece 1	6·8788 c.c.	6·8885 c.c.
2	6·8085	6·8178
3	6·8037	6·8157
4	6·6622	6·6601
5	7·5605	7·5563
6	7·4982	7·4948
7	7·7373	7·7385
8	6·7616	6·7695

It will be seen from these results that the two methods of measuring the expansion give closely agreeing results with the same piece of rubber, and are therefore reliable methods of measurement, but that the volume attained by different pieces of rubber from the same piece of tubing are widely different, probably owing to variation in the extent to which the rubber has been vulcanised. It is therefore evident that any change of volume of the expanded rubber due to the osmotic pressure of substances subsequently added to the carbon bisulphide would not be comparable if different pieces of rubber were used.

Experiments were next made to see if the same piece of rubber could be used consecutively, or whether the elasticity changed each time it was expanded with carbon bisulphide. For the purpose a piece of tubing was placed in carbon bisulphide until expanded, and the expansion was then determined by Method B. It was then suspended in air and left until the carbon bisulphide had completely evaporated, again placed in carbon bisulphide, and the expansion determined, and so on.

Weight of rubber - - ·7385 grm.

Volume (cal. on 1 c.c.) after 1st treatment with CS_2, 6·7616 cc.
" " " 2nd " " 6·8054
" " " 3rd " " 6·8657
" " " 4th " " 6·9685

Weight of rubber after the four treatments - - ·7165 grm.

It is evident that the volume elasticity of the rubber is not constant, even for the same piece, but decreases at each treatment with carbon

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bisulphide; a result which is doubtless due to the slow solvent effect of the carbon bisulphide, the rubber having lost 2·9 per cent. during the four treatments.

In order to make sure that the expansion of the rubber had practically ceased at the end of the time allowed for each experiment (24 hours), a sample was left in carbon bisulphide and weighed from day to day. The following are the results :—

Volume (cal. on 1 c.c.) after 24 hours - - -	7·5293 c.c.
„ „ „ 96 „ - - -	7·5432

Another sample changed in volume from 7·6453 to 7·7365 in three weeks. The vulcanised rubber is therefore practically insoluble, at any rate in a limited quantity (12 c.c.) of carbon bisulphide.

Since the elasticity of the rubber is constant only whilst it remains distended, and since it cannot be again brought to the same condition in a second experiment, some means was sought of expressing the results so that they might be comparable. The equation for volume elasticity is $P = k\frac{v}{V}$, where P is the pressure causing change of volume, V the initial volume of the body, and v the change of volume under the influence of the pressure; and it was thought that if the change of volume produced by diffusing substances was expressed in terms of the original volume of the expanded rubber, the results would be comparable for small values of "v" even if the size and elasticity of the pieces of rubber varied. The nature of the curves obtained have borne out this conclusion.

Method of Experiment.— Several methods of determining change of volume of rubber under the influence of osmotic pressure were tried. The following appeared the most satisfactory. A piece of ¼-inch tubing 1 inch long is weighed and its volume calculated from the specific gravity of the sample. It is then placed in a weighed corked test-tube, 12 c.c. of carbon bisulphide are added, and the rubber is left for 24 hours to expand. At the end of this time it is hooked out and its volume is determined by Method B. The rubber is then returned to the test-tube, and the whole is weighed. The weight less that of the test-tube and original rubber gives the weight of the carbon bisulphide. A small proportion (0·5 cc., for instance) of the substance whose osmotic pressure is to be measured is next added, and the whole again weighed. The liquid is well mixed and the rubber left in it for 24 hours to undergo any further change of volume due to the osmotic pressure of the added substance. It is then removed, and its volume and specific gravity determined by means of Method A. From its specific gravity the proportion of the added substance within the rubber can be calculated, and this deducted from the total amount taken gives the proportion of substance in the liquid outside the rubber. An example in which acetone was the substance under examination will serve to make the method clearer.

Data

Weight of rubber - - - - - - - - - -	·6190
Wt. of test-tube + rubber - - - - - - - -	9·7540
Wt. of rubber (expanded with CS_2) + w.-tube (1) - -	16·7600
„ „ „ „ „ (2) - -	16·7610
Wt. of test-tube + rubber + CS_2 - - - - - -	24·6400
„ „ „ „ + acetone (0·5 c.c.) - -	25·0650
Wt. of rubber (expanded with CS_2 + acetone) (1) - -	16·8425
„ „ „ „ (2) - -	16·8360
„ in water - - - - - - - - -	30·6385
Wt. of weighing-tube - - - - - - - - -	11·3475
„ „ + water (14° C.) - - - - -	29·6930
Sp. gr. CS_2 $\frac{10^v}{14}$ - - - - - - - - - -	1·2723
„ acetone $\frac{10^v}{14}$ - - - - - - - - - -	·8024

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Calculations

Wt. of rubber taken	·6190
Vol. „ (calc.)	·6602

(1) Expansion with CS_2 only :—

Wt. of w.-tube + expanded rubber	16·7610
	11·3475
	5·4135
	·6190
Wt. of absorbed CS_2	4·7945
Vol. (calc.)	3·7686
	·6602
Vol. of expanded rubber	4·4288

(2) Expansion with CS_2 + acetone :—

Wt. of tube + expanded rubber	16·8360
	11·3475
	5·4885
	29·6930
	35·1815
	30·6385
Vol. of expanded rubber	4·5430
	·6602
Vol. of CS_2 + acetone in rubber	3·8828
Wt. of expanded rubber	5·4885
	·6190
Wt. of CS_2 + acetone in rubber	4·8695

It is evident from the above calculations that the expanded rubber has changed in volume from 4·4288 c.c. to 4·5430 c.c. under the influence of the acetone. Of the latter a portion is within the rubber, the rest without. Let w and w' be the weights of acetone and carbon bisulphide respectively in the rubber, and d and d' their densities, then

$$w + w' = 4 \cdot 8695,$$

$$\frac{w}{d} + \frac{w'}{d'} = 3 \cdot 8828.$$

From these equations, wt. of acetone in rubber = ·1200,
whence grm.-mols. per c.c. of rubber = ·00046.

The composition of the fluid outside the expanded rubber is easily calculated as follows :—

	25·0650
	24·6400
Wt. of acetone taken	·4250
„ acetone in rubber	·1200
Wt. of acetone outside rubber	·3050
Vol. „ „	·3801

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	24·6400
	9·7540
Wt. of CS_2 taken	14·8860
„ CS_2 in rubber	4·7495
Wt. of CS_2 outside rubber	10·1365
Vol. „ „	7·9671
	·3801
Vol. of liquid outside rubber	8·3472
Grm.-mols. acetone per c.c. of fluid outside the expanded rubber	·00063

We find, then, from the above set of experiments, that a certain piece of rubber expands to a volume of 4·4288 c.c. when placed in carbon bisulphide only, but to a volume of 4·5430 c.c. when placed in a mixture of carbon bisulphide and acetone, there being ·00046 grm.-molecules of acetone per c.c. inside the rubber, and ·00063 grm.-mols. per c.c. outside. Now in order to make several such results comparable, the first volume is called 100. The second then becomes 102·58, and 2·58 per cent. is the expansion produced by the acetone under the given distribution.

The chief difficulty in the experimental method on which the above results are based lies in getting the expanded rubber into the weighing-bottle in an exactly dry condition. If the rubber is exposed too much to the air in its passage from the test-tube there is a decided loss of carbon bisulphide and consequent contraction, whilst if it is dropped into the bottle in a distinctly wet condition, the filter-paper with which the latter is lined fails to remove the whole of the adhering fluid. With care consecutive weighings may be within ·01 grm. of one another. This would amount to an error of about 0·4 per cent. of the volume of the expanded rubber. As there are two determinations of volume for each set of results, the error may disappear or it may amount to 0·8 per cent. The calculations have been made on the assumption that there is no change of volume when organic liquids are mixed. This is probably approximately true when the proportion of one constituent is small (see later). I have already shown that the volume of rubber expanded with carbon bisulphide is made up of the volume of the original rubber plus that of the absorbed carbon bisulphide.

In the experiments substances were chosen whose specific gravities differed largely from that of carbon bisulphide, so that the composition of the fluid mixture within the rubber might be calculated with tolerable accuracy from its specific gravity. When now a series of experiments were made with gradually increasing quantities of acetone, the following results were obtained :—

Vol. of expanded rubber.	Grm.-mols. acetone inside.	Grm.-mols. acetone outside.
100	0	0
102·58	·00046	·00063
103·76	89	110
104·14	178	199
100·57	259	321
86·93	344	478
71·52	396	612
58·76	394	717
32·77	339	999

If these results are plotted so as to make the number of grm.-mols. per c.c. the abscissæ and the volumes the ordinates, two curves are obtained (Fig. 1) which nearly coincide at first but rapidly diverge as the volume of the rubber becomes less.

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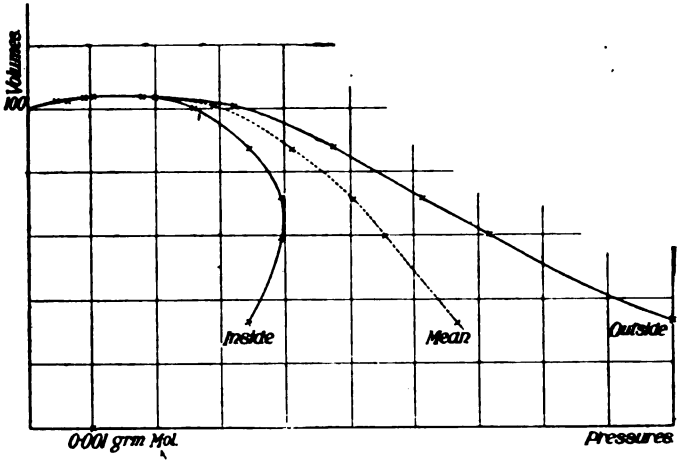
FIG. 1.—*Acetone. Constituents per cc. Inside and Outside.*



The peculiar shape of the curve representing the proportion of acetone inside the expanded rubber is evidently due to the fact that the relative space occupied by the rubber itself increases as the volume of the rubber decreases, hence there is less space for the fluid mixture within the rubber; moreover, as there is no affinity between the acetone and the rubber (acetone has little power *per se* to expand rubber) the former accumulates in the fluid outside. If the mean be taken between the two curves a new curve is obtained, the lower portion of which is a straight line, and which appears to be parabolic. It agrees well in its early part with the equation

$$p - ap^2 = kv,$$

where p is the mean number of grm.-mols. of acetone per c.c. inside and outside the rubber, v is the change of volume produced by the acetone, and a and k are constants. This is shown by the following calculated results:—

$a = 333 \cdot 14.$ $k = \cdot 000172.$

Grm.-mols. (mean) per c.c.	Vol.	Do. cal.
·00054	102·58	—
99	103·76	103·86
188	104·14	104·08
290	100·57	—
411	86·93	91·20
504	71·52	80·15
555	58·76	72·67
669	32·77	47·68

This result is interesting in view of the recent work on the depression of the freezing point, &c. For with very small percentages of acetone the term ap^2 would disappear, and the equation would become $p = kv$; or the *increase* of volume is at first proportional to the amount of dissolved substance. Results to follow will show that it is proportional to the number of grm.-molecules, so that we have here an exact analogue of Raoult's well-known law. Next with regard to the term ap^2, which becomes significant when larger quantities of acetone are present. Taking for granted that the change in volume of the rubber really represents the osmotic pressure of the dissolved substance, the expansion would at first be proportional to the number of molecules of acetone present, since the latter would at first exert a pressure equivalent to that of a perfect gas, but as the quantity of acetone increased the attraction between its molecules would become sensible and the pressure would begin to decrease.

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The negative pressure due to the mutual attraction of the molecules of a gas varies according to van der Waals inversely as the square of the volume, that is directly as the square of the number of molecules in unit volume: hence the term ap^2 may be considered to represent the loss in pressure of the acetone due to the mutual attraction of its molecules.

Van der Waals' equation also involves the space $(V - b)$ surrounding the molecules of a gas. In the case of liquids, however, this is constant for the same liquid at the same temperature, and would remain so on dissolving the liquid in another one since the changes of volume on mixing organic liquids are so small as to be negligible. In fact, we may suppose that the molecules of a liquid are pressed so closely together that they do not readily undergo any further change, the molecular volumes of organic liquids calculated from their specific gravities being much smaller than the values calculated from "b" in van der Waals' formula. The force represented by "a" in the latter formula may, on the other hand, remain intact in mixed liquids, unless indeed the intervening liquid acts in some way as a dielectric, and we may therefore expect that the osmotic pressure will be represented by a quadratic expression. In giving the above interpretation to the equation $p - ap^2 = kv$, the change of volume of the expanded rubber has been supposed to be proportional to the total osmotic pressure of the dissolved substance, or, in other words, that the osmotic pressure of the dissolved substance is balanced by the volume-elasticity of the rubber. The equation for the latter is $P = k\frac{v}{V}$, but as in our case V is always 100, the equation becomes $P = Kv$.

It is now necessary to show that the equation for acetone is generally true for dissolved substances. The substance next taken was benzene, which differs from acetone in having a power of expanding rubber nearly equal to that of carbon bisulphide. The character of the curve, however, remains unaltered. The following are the results:—

Vol. of expanded rubber.	Grm.-mols. benzene, per c.c. inside.	Do. outside.
100	0·	0·
102·62	·00043	·00045
103·24	82	77
104·54	126	132
105·31	141	151
105·65	189	189
106·13	219	225
105·82	234	241
106·40	257	272
106·82	283	297
107·07	304	322
107·29	331	356

The values calculated for the equation $p - ap^2 = kv$ give the following results:—

$a = 203·9.$ $k = ·000205.$

Grm.-mols. per c.c. (mean).	Vol.	Do. cal.
·00044	102·62	101·96
79	103·24	---
129	104·54	104·65
146	105·31	105·01
189	105·65	—
222	106·13	105·94
237	105·82	105·99
264	106·40	105·96
290	106·82	105·79
313	107·07	105·54
343	107·29	105·04

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The first volume being undoubtedly erroneous the values for a and k have been calculated from points 2 and 5. The curve would terminate at a volume of 91·41 if continued far enough, this being the volume which rubber attains when placed in benzene alone. It lies, therefore, for the most part above the line of initial volume, and there is a much closer coincidence between the observed and calculated volumes than in the case of acetone. In other words, the attraction between the molecules of benzene is partially balanced by the attraction of the rubber for the benzene, the value for "a" is consequently much smaller, and the benzene behaves as a perfect gas for a greater distance along the curve. We may note here the interesting fact that a mixture of carbon bisulphide and benzene has a greater effect in expanding rubber than either constituent alone, the maximum volume with a mixture being about 107, whilst carbon bisulphide and benzene alone produce volumes of 100 and 91·41 respectively. The same thing is observed with chloroform and ether, which, like benzene, are soluble in rubber. This fact would seem to explain the superiority of mixed solvents over single ones in many cases, especially in the solution of resins, which are to some extent colloids. Colloidal solutions are always characterised by great viscosity, and it is doubtful if they are true solutions. Possibly the elasticity of a "soluble" colloid is so small that a balance between the osmotic pressure of the solvent and the elasticity is not easily reached, and the colloid therefore expands indefinitely.

Chloroform.—The following values were obtained :—

Vol.	Grm.-mols. per c.c. inside.	Do. outside.
102·55	·00025	·00068
104·29	50	110
106·30	96	169
108·52	159	244
109·54	190	269
111·06	217	313
111·21	241	328

Calculated values for the equation $p - ap^2 = kv$:—

$a = 126·9.$ $k = ·00017.$

Grm.-mols. (mean) per c.c.	Vol.	Co. cal.
·00046	102·55	—
80	104·29	104·23
132	106·30	106·46
201	108·52	108·81
228	109·54	—
265	111·06	110·35
284	111·21	110·69

The curve here is similar to that of benzene, and agrees well with the equation $p - ap^2 = kv$. The volume produced by chloroform alone is 112·9, hence the curve never dips below the line of initial volume.

Ether.—The following values were obtained :—

Vol.	Grm.-mols. per c.c. inside.	Do. outside.
102·23	·00037	·00037
103·58	62	68
104·75	95	107
105·47	117	134
106·83	146	167
107·83	165	192
107·94	189	219
107·73	205	239

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Calculated values for the equation $p - ap^2 = kv$:—

$a = 210 \cdot 13.$ $k = \cdot 000154.$

Grm.-mols. per cc. (mean).	Vol.	Do. cal.
·00037	102·23	—
68	103·58	103·79
101	104·75	105·17
125	105·47	105·99
156	106·83	—
178	107·83	107·25
204	107·94	107·58
222	107·73	107·70

Two more substances were examined, namely, acetic ethyl ether and malonic ethyl ether. These substances, like acetone, have little power of expanding rubber by themselves, hence the curve soon reaches a maximum.

Acetic Ether. Vol.	Grm.-mols per c.c. inside.	Do. outside.
102·19	·00043	·00040
103·72	79	71
105·44	203	205
105·16	233	252
101·14	300	336

Calculated values for the equation $p - ap^2 = kv$:—

$a = 266 \cdot 3.$ $k = \cdot 000167.$

Grm.-mols. per c.c. (mean.)	Vol.	Do. cal.
·00041	102·19	—
75	103·72	103·60
204	105·44	105·59
242	105·16	—
318	101·14	102·92

Malonic Ether. Vol.	Grm.-mols. per c.c. inside.	Do. outside.
101·84	·00064	·00038
100·95	80	63
99·61	95	94
97·29	117	106
94·61	138	130

Values calculated for the equation $p - ap^2 = kv$:—

$a = 1152.$ $k = \cdot 00011.$

Grm.-mols. (mean) per c.c.	Vol.	Do. cal.
·00051	101·84	—
71	100·95	101·13
94	99·61	99·32
112	97·29	—
134	94·61	93·62

The observed volumes for these substances agree at first with those calculated, but soon diverge, as with acetone. The value for "a" is particularly large with malonic ether, as might be expected from its high boiling-point.

In measuring the osmotic pressures of the preceding seven substances, the initial state of the rubber has been its state when fully expanded with carbon bisulphide, it being assumed that the changes of volume were entirely due to the osmotic pressure of the dissolved substances, this pressure being eventually balanced by the volume-elasticity of the distended rubber; and that the carbon bisulphide simply served as a convenient vehicle for the introduction of the diffusing substance in a

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molecular condition. In order to prove this a set of experiments were made in which the rubber was first distended with benzene. Small proportions of carbon bisulphide were then added, and any change of volume determined. The initial volume was in this case called 91·41, this being the volume produced by benzene alone when the volume produced by carbon bisulphide alone equals 100. The following results were obtained :—

Carbon bisulphide in Benzene.

Vol.	Grm.-mols. CS_2 per c.c. inside.	Do. outside.
91·41	0·	0·
95·29	·00063	·00081
96·70	103	130
98·22	144	182
99·51	191	237

Values calculated for equation $p - ap^2 = kv$:—

$a = 180·3$. $k = ·00016$.

Grm.-mols. (mean).	Vol.	Do. cal.
·00072	95·29	—
116	96·70	97·06
163	98·22	98·50
214	99·51	

It will be seen that the observed values agree well with the equation $p - ap^2 = kv$. The values for a and k are also comparable with those obtained for the previous substances. Since the initial volume of the rubber is here 91·41 whilst in the previous sets of experiments it was 100, these results show that the swollen rubber really obeys the law for volume elasticity, at any rate for small (10 per cent.) charges of volume. I hope to examine this matter more fully.

Values for "a."—In explaining the equation $p - ap^2 = kv$ I have supposed "a" to represent the same value as it does in van der Waals' equation for gases, and it might at first be expected that it would be identical with it. It is found, however, that all liquids, except perhaps alcohol,* have a slight power of their own of diffusing into and expanding rubber, hence we must suppose that there is a slight attraction between the rubber and the molecules of the substance. The effect of such an attraction would be to spread the substance evenly throughout the rubber, and this force of attraction may therefore be supposed to act from within outwards and to oppose the mutual attraction of the molecules of the dissolved substance. The equation now becomes

$$p - (a - A)p^2 = kv$$

where "a" is van der Waals' value, and A the force of attraction between the rubber and the substance. This view is supported by the fact that all the substances examined conform to the expression $p - ap^2 = kv$ whether their solubility in rubber is great or small, and also *that the divergence of the value "a" from van der Waals' value becomes greater as the solubility of the substance in rubber increases.* This is shown by the following table :—

Values for "a."	From van der Waals' equation (cal. on 1 c.c.).	Observed.	Max. vol.
Acetone	611·0	333·1	16·9
Acetic ether	778·8	266·3	22·7
Ether	725·1	210·1	54·4
Benzene	980·2	203·9	91·4
Chloroform	642·3	126·9	111·4
Carbon bisulphide (in benzene)	490·1	180·3	100·0

* Experiments with alcohol were vitiated owing to traces of moisture which it contained, and which caused it to separate in globules from the carbon bisulphide after some time.

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The values for "a" in van der Waals' equation are taken from Ostwald's "Outlines of General Chemistry," p. 87. His values have been multiplied by 22380, as in these experiments the unit of volume has been 1 c.c. instead of 1 litre. The maximum volume mentioned is the volume attained by rubber when placed in the liquid alone, the volume attained by the same piece of rubber when placed in carbon bisulphide being called 100. This maximum volume represents the solubility of the substance in rubber, and is taken as a rough measure of the attraction between the rubber and the liquid.

Now it will be seen that the observed value for "a" is always less than van der Waals' value, as is required by our theory, and that the ratio between them is always greater, the greater the attraction between the rubber and the substance. This is more clearly shown in the following table :—

	Van der Waals' value. / Observed value.	Max. vol.
Acetone	1·83	16·9
Acetic ether	2·92	22·7
Ether	3·45	54·4
Benzene	4·81	91·4
Chloroform	5·06	111·4
Carbon bisulphide (in benzene)	2·71	100·0

So that in explaining the value for "a," I suppose the molecules to be acted upon by two opposing forces—their mutual attraction, which is alone considered in van der Waals' equation, and the attraction between them and the mass of the surrounding matter, in virtue of which they diffuse. The latter force is probably due to both the rubber and the carbon bisulphide in which the substance is dissolved. This view is supported by the last result in the above tables, in which the substance (carbon bisulphide) was dissolved in benzene. The ratio between the two values for "a" is not now in line with the others. The effect of the rubber on the value for "a" might be reduced to a minimum by using a very slightly vulcanised specimen. The initial volume of the rubber would then be very large, and as a consequence the mass of the rubber per unit volume would be very small. The divergence of "a" from van der Waals' value would then be due entirely to the affinity of the solvent for the dissolved substance. I hope to make experiments on this point. The values for "a" obtained in this way would probably be less than those of van der Waals.

Values for "k."—The following are these values for the substances examined :—

Chloroform	·000170
Benzene	205
Ether	154
Acetic ether	167
Acetone	172
Carbon bisulphide	162
Malonic ether	114

These values should probably be nearly identical except in the case of malonic ether. In order to get a close value for k, it will be necessary to make a number of determinations of its value at an early part of the curve and take the mean, since the experimental error is greatest when the expansions are small. According to van der Waals' equation the pressure of a gas is inversely as $(V - b)$, the empty space surrounding the molecule. This would be constant for the same liquid as already pointed out, but would vary with different liquids, would be greater the greater the molecular volume and would probably be nearly proportional to it. Hence, since the molecular volume of malonic ether is nearly double of that of the other substances, its osmotic pressure is only

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one half. It must be confessed that this explanation is not very satisfactory, the more so as nothing analogous is met with in the laws regulating the depression of the freezing-point, &c. It may be noted that the initial distribution of the substance inside and outside the rubber is very unequal in the case of malonic ether.

Distribution of Diffusing Substances inside and outside the Colloid.—Hitherto we have considered the curve produced by taking the *mean* number of grm.-molecules per c.c inside and outside the colloid for the abscissæ and the volumes of the colloid for the ordinates, as it was found that the most regular curve was obtained in this way in the original experiment with acetone. Moreover, the two curves (Fig. 1) representing the distribution of acetone inside and outside the colloid would eventually coincide with the mean curve when the colloid is infinitely expanded, that is when the conditions inside and outside the colloid are identical. For this reason the mean curve was considered best to represent the osmotic properties of the substance under examination. In order to investigate the unequal distribution of the diffusing substance produced by the presence of the colloid, it was though best to make use of the above two curves instead of attempting to apply ordinary diffusion data, as the rate of expansion of rubber when placed in carbon bisulphide could not be made to conform to Fick's law (*see* later). If the curves in question be examined, it will be seen that they run alongside of the mean curve for a considerable distance and do not differ from it greatly in character; and it will be found that they agree closely at first with the equation $p - ap^2 = kv$, "a" and "k" being different for the "inside" and "outside" curve. This is best seen with those substances—ether, benzene, and chloroform—which are themselves soluble in rubber and whose curves lie mostly above the line of initial volume. The following are the results :—

Benzene.—Inside.

$a = 191{\cdot}8$. $k = {\cdot}00021$

Grm.-mols. per c.c inside	Vol.	Do. cal.
·00043	102·62	101·85
82	103·24	—
126	104·54	104·46
141	105·31	104·82
189	105·65	—
219	106·13	105·95
234	105·82	106·04
257	106·40	106·11
283	106·82	106·07
304	107·07	105·94
331	107·29	105·67

Outside.

$a = 215{\cdot}2$. $k = {\cdot}000198$

Grm.-mols. per c.c outside.	Vol.	Do. cal.
·00045	102·62	102·04
77	103·24	—
132	104·54	104·76
151	105·31	105·14
189	105·65	—
225	106·13	105·85
241	105·82	105·84
272	106·40	105·68
297	106·82	105·40
322	107·07	104·99
356	107·29	104·20

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Chloroform.—Inside.

$a = 280 \cdot 8$. $k = \cdot 000103$.

Grm.-mols. per c.c. inside.	Vol.	Do. cal.
·00025	102·55	—
50	104·29	104·19
96	106·30	106·80
159	108·52	—
190	109·54	108·60
217	111·06	108·24
241	111·21	107·58

Outside.

$a = 26 \cdot 52$. $k = \cdot 00026$.

Grm.-mols. per c.c. outside.	Vol.	Do. cal.
·00068	102·55	—
110	104·29	104·07
169	106·30	106·15
244	108·52	108·72
269	109·54	—
313	111·06	110·96
328	111·21	111·44

Ether.—Inside.

$a = 187 \cdot 7$. $k = \cdot 000155$.

Grm.-mols. per c.c. inside.	Vol.	Do. cal.
·00037	102·23	—
62	103·58	103·53
95	104·75	105·03
117	105·47	105·88
146	106·83	—
165	107·83	107·34
189	107·94	107·86
205	107·73	108·13

Outside.

$a = 224 \cdot 4$. $k = \cdot 000153$.

Grm.-mols. per c.c. outside.	Vol.	Do. cal.
·00037	102·23	—
68	103·58	103·77
107	104·75	105·32
134	105·47	106·13
167	106·83	—
192	107·83	107·15
219	107·94	107·29
239	107·73	107·25

We can now calculate the distribution of the diffusing substance for any given volume; for let $p - ap = kv$ represent the relation between volume and grm.-mols. per c.c. inside the colloid, and $p' - a'p'^2 = k'v$ represent the relation outside the colloid; then

$$\frac{p - ap^2}{p' - a'p'^2} = \frac{k}{k'}.$$

Now when p and p'^2 are both very small the second terms vanish and the expression becomes

$$\frac{p}{p'} = \frac{k}{k'} = \mathrm{K}.$$

This is Henry's law for gases.

In our arrangement we have benzene, &c., dissolved in carbon bisulphide for the gas, the difference in density between the two parts which causes the unequal distribution being brought about by the presence

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of the swollen colloid. In the case of a gas dissolved in water, the difference in density is due to the different states (vapour and liquid) in which the solvent exists. This difference will cease in the former case when the colloid dissolves, and in the latter when the critical temperature is reached.

If the quantities of dissolved substance are larger, we have

$$\frac{p}{p'} = \frac{a'}{a} \cdot \frac{1 \pm \sqrt{4akv}}{1 \pm \sqrt{4a'k'v}};$$

or the distribution of the gases is no longer a constant ratio but becomes a function of the increase in volume of the solvent. The vapour tension of solutions of ammonia, &c., might perhaps be investigated by means of this equation, as also that of mixed liquids.

The difference in the values for a and a' is evidently due to the attraction of the colloid for the dissolved substance, or rather to the difference in attraction of the colloid on the one hand and the solvent on the other. There are not sufficient data to explain the ratio $\frac{k}{k'}$. In the case of benzene and ether this ratio is equal to unity, and these two substances have molecular weights equal to that of the solvent (CS_2). It will be seen that the values of a and k for benzene are nearly equal to those of a' and k' respectively: hence the distribution remains constant, as required by the above formula. This is seen in the following table.

Benzine.—Ratio of grm.-mols. per c.c. inside and outside the colloid.

Vol.	Benzene inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
100	0·	0·	
102·62	·00043	·00045	1·05
103·24	82	77	0·94
104·54	126	132	1·04
105·31	141	151	1·06
105·65	189	189	1·00
106·13	219	225	1·03
105·82	234	241	1·03
106·40	257	272	1·06
106·82	283	297	1·05
107·07	304	322	1·06
107·29	331	356	1·07

Volume attained by Rubber when placed in single fluids.—These values have already been mentioned. They are easily obtained by placing rubber in carbon bisulphide for 24 hours and determining its volume by method B. The carbon bisulphide is then allowed to evaporate, and the rubber when quite dry is placed in the liquid under examination for 24 hours, and the volume calculated as before. Finally the rubber, after drying, is placed once more in carbon bisulphide and the volume attained again determined. The mean of the two volumes in carbon bisulphide is called 100, and the volume attained by the rubber when placed in the liquid under investigation is referred to this value. The following are the results:—

Carbon bisulphide	100·0
Acetone	16·9
Acetic ether	22·7
Ether	54·4
Benzene	91·4
Chloroform	111·4
Vol. of unswollen rubber (average)	13·3

Change of Volume on mixing Organic Liquids.—The calculations of the results in the preceding experiments have been made on the assumption that the change of volume on mixing organic liquids is negligible, at any

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rate when the proportion of one constituent is small. To prove this, mixtures were made with weighed quantities of alcohol and carbon bisulphide, and the density of the mixture was determined. The number of grm.-molecules of alcohol per c.c. was then calculated (1) from the weighed quantities taken, on the assumption that no change of volume had taken place on mixing, (2) from the density of the fluid mixture. The following are the results:—

	Grm. mols. alcohol per c.c.	
	Actual.	Calculated.
Mixture 1 - - - -	·0001998	·0002005
„ 2 - - - -	5114	5138
„ 3 - - - -	8626	8675

Rate of Expansion.—Thus far the conditions under which the colloid has been examined have been statical, that is to say, the colloid has been placed in the mixed liquids and left until equilibrium has been established The simplest dynamical relationship is the rate of expansion of the colloid when placed in a single fluid. This is easily determined by placing a piece of weighed rubber in the liquid and transferring it at stated intervals into the paper-lined weighing-tube, in which it is then weighed after removing the paper (Method B). The total volume at the end of each period is easily calculated from the weight of the original rubber and that of the absorbed carbon bisulphide, on the assumption that the volumes are additive. This has already been proved to be the case. The expansion is at first very rapid, but soon decreases, and it was found to agree for a considerable distance with the equation $V = k \log t$, where V is the total volume at any moment, t the time elapsed, and k a constant. This is shown by the following results, the interval (about 3 minutes) required for each weighing not being included in the times stated.

Rate of Expansion with Carbon Bisulphide.

Vo. (cal. on 1 c.c. of rubber).	Time elapsed.	*k*.
1·0000	0 min.	—
2·3541	5 „	3·37
3·8198	15 „	3·25
4·9241	30 „	3·33
5·8771	60 „	3·31
6·2527	90 „	3·20
6·4079	120 „	3·08
6·5394	185 „	2·88
6·5615	245 „	2·75
6·5728 (max. vol. actual)	305 „	2·64

As the maximum volume is approached the value for k rapidly drops, either because the limit of elasticity of the rubber is reached or because the osmotic pressure of the diffusing liquid becomes balanced by the volume elasticity of the rubber. Since different maximum volumes are obtained with different substances (relative max. vol. with carbon bisulphide = 100, with chloroform = 112, with benzene = 91, and with ether = 54), the former conclusion cannot be correct, hence the latter conclusion must be accepted. If the rubber were unvulcanised it would dissolve completely in the carbon bisulphide; hence we must suppose that the coefficient of volume elasticity of unvulcanised rubber gradually becomes less as the volume increases, or that it is so small that it never balances the osmotic pressure, or only does so when the volume has become very great. The latter conclusion seems the more probable. The rapid drop in the value of k in the above results could be explained by the supposition that k represents a molecular friction or a sorting of the diffusing substance, since the friction would become *nil* when the osmotic

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pressure became balanced by the elasticity of the colloid and the latter ceased to expand.

In another series of experiments, in which the weighings were made at shorter intervals, the following results were obtained, the time of weighing not being included in the times stated :—

Vol. (cal. on 1 c.c.).	Time elapsed.	K.
1·0000	0 min.	—
2·1355	5 ,,	3·06
3·0061	10 ,,	3·01
3·6988	15 ,,	3·14
4·2141	20 ,,	3·24
4·6569	25 ,,	3·33
5·0204	30 ,,	3·40
5·2990	35 ,,	3·43
5·7507	50 ,,	3·38
6·0510	65 ,,	3·34
6·2555	80 ,,	3·29
6·4797	110 ,,	3·17
6·5787	140 ,,	3·07
6·6674	200 ,,	2·90
6·6843	280 ,,	2·73

The values for k are probably not so accurate in this as in the previous series, since during the weighing the carbon bisulphide would tend to become equalised through the mass of the colloid, and the conditions would be proportionately disturbed. A linear measurement of the expanding colloid would give more accurate results, as it could be made without disturbing the conditions of the experiment.

The equation $V = k \log t$, representing the expansion of vulcanised caoutchouc when placed in carbon bisulphide, does not seem to be related to Fick's law for diffusion. That the conditions of the diffusion of carbon bisulphide into rubber are different to those of the diffusion of one liquid into another, is evident from the fact that the volume attained by the rubber is independent of the amount of carbon bisulphide taken, provided the latter is in excess. The diffusion of the carbon bisulphide continues until its pressure is balanced by the volume elasticity of the colloid, so that only one of the constituents diffuses. When ether is placed in contact with water, on the other hand, they each diffuse into one another. The regularity of the diffusion which allows it to be represented by the above equation is probably due to the fact that with pieces of tubing two parallel surfaces are presented to the liquid, the surfaces of the ends being negligible. There is therefore very little strain in the rubber. With pieces of rubber cord the same regularity was not observed. If similar conditions to the above hold for "soluble" colloids, then we can say that their slow diffusion is due to the opposition offered to the diffusion of the solvent into their substance by their volume elasticity instead of referring it to their large molecular weight. If the volume elasticity is small the colloid will dissolve in all proportions.

Relative Values of "k" for different Substances.—In order to find the relative values for "k" for different substances in the equation $V = k \log t$, the following method was devised in order to correct the variable value for the elasticity of the colloid. A piece of rubber tubing was weighed after ½ hour in carbon bisulphide, and the value k_1 calculated. It was exposed to the air until the carbon bisulphide had completely evaporated, and was then placed for ½ hour in the liquid under examination, weighed, and the value k_x calculated. Lastly, it was again dried, and placed once more in carbon bisulphide, and the value k_2 calculated. It is evident that the rate of expansion in the liquid x will be to the rate of expansion in carbon bisulphide as $\frac{k_x}{\frac{1}{2}(k_1 + k_2)}$. In this way the relative

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velocities of diffusion of carbon bisulphide, ethyl iodide, chloroform, benzene, and ether were determined. The following are the results :—

	k. For 30 min.	k. For 90 min.
Carbon bisulphide	1·000	1·000
Chloroform	·838	·976
Ethyl iodide	·668	·794
Benzene	·655	·754
Ether	·570	·553

Of these substances two are heavier than carbon bisulphide and two are lighter. Now the initial velocities of diffusion of the denser substances are *inversely* as their densities as compared with that of carbon bisulphide, whilst the velocities of the lighter substances are *directly* as their densities. Thus :—

	k (30 min.).	$\frac{\text{Density of } CS_2}{\text{Density of subst.}}$	$\frac{\text{Density of subst.}}{\text{Density of } CS_2}$
Carbon bisulphide	1·000	1·000	1·000
Chloroform	·838	·848	
Ethyl iodide	·668	·669	
Benzene	·655	—	·686
Ether	·570	—	·568

So that if the densities of the substances be plotted as abscissæ and the values for k as ordinates, a curve will be obtained which will rise rapidly to a maximum for carbon bisulphide and then gradually decrease. This result is very remarkable. It is difficult to see what property reaches a maximum in carbon bisulphide.

A more understandable relation is got by comparing the mean velocities of diffusion with the molecular volumes. It will be found that they are inversely as the latter. Thus :—

	(mean).	$\frac{\text{Mol. vol. of subst.}}{\text{Mol. vol. of } CS_2}$
Carbon bisulphide	1·000	1·000
Chloroform	·907	·910
Ethyl iodide	·731	·784
Benzene	·704	·689
Ether	·561	·639
Turpentine	·361	·344

but the agreement is not so close here as in the relation involving the densities.

The two relations given above, one referring to the density of the substance and the other to the molecular volume, cannot both hold good for all substances, since by polymerising a substance the molecular volume may be increased indefinitely, whilst little change is produced in the density. As a matter of fact, the value for k for turpentine is in accord with its molecular volume, whilst it has only one-half the value it should have if the relation for densities held good, thus

$$\frac{\text{density of turpentine}}{\text{density of } CS_2} = \cdot 685.$$

At this rate isoprene C_5H_8 would conform to both relations.

This would seem to show that the relation involving the densities holds only for the simplest types. According to the second relation found, substances diffuse into rubber the more readily the smaller their molecular volumes, a result which one might expect. It is true that no note is here taken of the configuration of the molecule, which is generally considered to have an important influence on the solution of substances, but this factor may be involved in the *affinity* between the rubber and the substance.

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This affinity is large in the case of the five substances considered, since they all expand rubber to a large extent, and it is obvious that the above laws can only hold good when the substance dissolves freely in the rubber. For instance, alcohol has about the same molecular volume as carbon bisulphide, but does not penetrate rubber at all; acetone, with a slightly larger volume, dissolves in rubber only with extreme slowness, producing a slight increase in volume. We may say, then, that when the force urging the molecules is large, they enter with a speed inversely as their molecular volumes, or, in other words, that the rubber seems to act as a sort of sieve. The above method of weighing a piece of rubber tubing after it has remained in a liquid for a given time, and calculating the velocity of diffusion, may prove a valuable means of determining molecular volumes, and hence of molecular weights, and could be applied to a number of inorganic liquids such as the chlorides of boron, silicon, tin, phosphorus, arsenic, and antimony.

The above relation for the diffusion of liquids into rubber involving the density is in accord with Graham's rates of "transpiration" of gases with the remarkable difference that the law is reversed; that is, when the gas is lighter than the reference substance (oxygen) its speed of transpiration is *inversely* as the densities, and *vice versâ*. Thus:—

	Rate of Transpiration (Graham).	Density of subst. / Density of Oxygen.	Density of Oxygen. / Density of subst.
Oxygen	1·0000	1·0000	1·0000
Air	1·1074	—	1·1056
Nitrogen	1·141	—	1·143
Nitric oxide	1·141	—	1·066
Carbonic oxide	1·145	—	1·143
Nitrous oxide	1·335	1·375	
Hydrochloric acid	1·358	1·141	
Carbonic anhydride	1·370	1·375	
Chlorine	1·500	2·219	
Sulphurous anhydride	1·538	2·000	
Hydrogen sulphide	1·614	1·062	
Methane	1·815	—	2·000
Ammonia	1·955	—	1·882
Ethylene	1·980	—	1·143
Hydrogen	2·288	—	16·
Carbon bisulphide (vapour)	1·614	2·375	
Methyl Chloride	1·826	1·578	
Ethyl „	2·005	2·015	
Methyl oxide	2·072	1·437	
Ethyl „	2·273	2·922	

It will be seen that the relation holds good for the more permanent gases—oxygen, nitrogen, nitric oxide, carbonic oxide, nitrous oxide, carbonic anhydride, and ethyl chloride; whilst of the remaining gases, those near their liquefying points, viz., chlorine, sulphurous anhydride, ether, and carbon bisulphide, have rates of transpiration less than the calculated values. This would follow from the law which I have found for the transpiration of liquids (into rubber), for the first three substances when liquefied would probably have rates of transpiration much smaller than unity. So that we have here evidence of incipient liquefaction, just as we should have if we were to examine these substances in relation to Boyle's law.

The substances now left are hydrochloric acid, hydrogen sulphide, methane, ammonia, ethylene, methyl chloride and oxide. These all show rates of transpiration greater than the calculated values except methane. They are all compounds of hydrogen or methyl, and it will be noted that the rate of transpiration of hydrogen is greater than that of any of the

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substances examined. This is in accordance with the fact that hydrogen is a gas "plus que parfait," that is, that its molecular volume (van der Waals' "*b*") is much greater than that of other gases. The same characteristic seems to apply to methyl.*

If we reverse the second law which I have found for liquids, it will stand "rates of transpiration are *directly* as the molecular volumes." On glancing over Graham's rates it will be seen that this is approximately the case, compounds of hydrogen and methyl excepted; that is, the rates of transpiration of gases increase with molecular complexity. If we knew more of the actual volumes of gaseous molecules (van der Waals' "*b*") we should be able to examine this relation more fully.

The consideration of the diffusion of liquids into rubber as a case of transpiration seems to be allowable, since gaseous transpiration is not confined to fine tubes, but was found by Bunsen to apply to ordinary gaseous diffusion when the diaphragm was thick, as when plugs of plaster of paris were used.

The standard substances, viz., oxygen in Graham's experiments on gases and carbon bisulphide in the above experiments with liquids, appear to be the substances which have the smallest molecular volumes in their respective states, viz., gas and liquid.

It is not easy to see why increase of molecular volume should increase the rate of transpiration of gases, except that the impacts would be more frequent, which would lead to an increased facility "in turning corners." That a highly tenuous gas has some difficulty in doing this seems to be proved by some recent experiments of Dewar, in which mercury vapour diffused from a small to a large bulb through a small aperture, both bulbs being vacuous, the presence of mercury vapour in the larger bulb being made evident by the application of a low temperature. The vapour passed with extreme slowness from one bulb to the other, although when the mercury was transferred to the large bulb a mirror was easily obtained by the application of liquid oxygen to the outside of the bulb. The interstices in rubber are probably much smaller than those in capillary tubes or plaster of paris, since transpiration phenomena cannot be obtained with gases through rubber. With such small interstices, smallness of molecular volume would be advantageous to diffusion. Moreover, the impacts of the molecules of liquids are so frequent that their ability to turn corners is practically infinite.

Referring once more to the transpiration of gases, we have the following values for density (mol. weight) and rates of transpiration :—

	Mol. weight.	Rate of transpiration (mol. vol.).
Nitrogen	28	1·141
Carbonic oxide	28	
Nitric „	30	
Oxygen	32	1·000
Nitrous oxide	44	1·335
Carbonic anhydride	44	
Ethyl chloride	64·5	2·005

It will be seen that with gradual increase of molecular weight the rate of transpiration falls to a minimum, and then again increases. If the molecular volumes (actual) are proportional to the rates of transpiration, then we have here something analogous to the relation of the atomic volumes of the elements to the atomic weights in each series of the periodic arrangement.

In comparing the transpiration of liquids and gases, it may be noted that the liquids enter the rubber in virtue of a "pull," whilst gases transpire through tubes in virtue of a "push." This difference may perhaps account for the inversion which has been described.

* Methyl compounds stand somewhat apart from their homologues in solubility and chemical properties. Thus methyl alcohol is insoluble in carbon bisulphide, its homologues are soluble.

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The above relations between velocity of diffusion and molecular volume for liquids will furnish a means of determining the distribution of the two liquids (carbon bisulphide and benzene, for instance) inside and outside the rubber in the statical experiments already described. For if rubber when placed in a liquid expands according to the equation $V = k \log t$, then it is reasonable to suppose that if the distended rubber were placed in some other liquid, which was continually renewed, it would contract along the same path and with corresponding speeds, that is, rapidly at first and afterwards more and more slowly, so that k would remain the same. Now let a piece of rubber be placed in a mixture of carbon bisulphide and benzene until equilibrium is reached, and let there be a c.c. of carbon bisulphide and b c.c of benzene per c.c. of *fluid* inside the rubber, and let there be a' c.c. and b' c.c. respectively outside the rubber, and let v_1 and v_2 be the molecular volumes of carbon bisulphide and benzene respectively. Then the velocity with which carbon bisulphide will diffuse in will be $\frac{a'}{v_1}$ and that at which it will diffuse out will be $\frac{a}{v_1}$, and since there is equilibrium $a' = a$. In the same way $b' = b$, that is, the density of the fluid will be the same inside and outside the rubber if the rates of diffusion are always inversely as the molecular volumes. This is the case with mixtures such as that of carbon bisulphide and benzene, in which both constituents enter the rubber freely "*per se*," but is not the case with mixtures such as that of carbon bisulphide and acetone. For acetone will penetrate rubber easily in the presence of carbon bisulphide, but will not do so by itself. These two cases are exemplified by the following results :—

Densities of fluid mixture inside and outside the colloid

Benzene and Carbon Bisulphide.

Vol.	Sp. gr. inside.	Sp. gr. outside.
100·00		1·2630 (carbon bisulphide alone).
102·62	1·2441	1·2461
103·24	1·2280	1·2345
104·54	1·2103	1·2149
105·31	1·2037	1·2079
105·65	1·1898	1·2000
106·13	1·1778	1·1874
105·82	1·1714	1·1817
106·40	1·1603	1·1687
106·82	1·1496	1·1598
107·07	1·1413	1·1511
107·29	1·1304	1·1390
99·51	·9198	·9233
98·22	·9068	·9103
96·70	·8957	·8978
95·29	·8847	·8864
91·41		·8671 (benzene alone).

Acetone and Carbon Bisulphide.

Vol.	Sp. gr. inside.	Sp. gr. outside.
100·00		1·2723 (carbon bisulphide alone).
102·58	1·2541	1·2508
103·76	1·2369	1·2350
104·14	1·2022	1·2045
100·57	1·1698	1·1632
86·93	1·1258	1·1020
71·52	1·0983	1·0564
58·76	1·0909	1·0203
32·77	1·0634	·9242

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If we compare the quantities of *carbon bisulphide* per c.c. of fluid mixture inside and outside the colloid, we shall see that the carbon bisulphide is at first practically "level," but afterwards it preponderates inside the rubber as the volume decreases.

Grm.-mols. of Carbon Bisulphide per c.c. of fluid mixture inside and outside the colloid

Carbon Bisulphide and Acetone.

Vol.	Grm.-mols. of carbon bisulphide per c.c. inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
102·58	·01609	·01598	·993
103·76	1548	1541	·995
104·14	1424	1433	1·006
100·57	1309	1286	·982
86·93	1168	1085	·929
71·52	1070	923	·862
58·76	1043	795	·762
32·77	945	453	·479

Carbon Bisulphide and Acetic Ether.

Vol.	Grm.-mols. per c.c. inside.	Do. outside.	Ratio $\frac{\text{outside.}}{\text{inside.}}$
102·19	·01593	·01609	1·010
103·72	1525	1558	1·021
105·44	1296	1342	1·036
105·16	1239	1264	1·020
101·14	1111	1129	1·016

In both these cases the proportion of carbon bisulphide inside the rubber is least when the volume of the latter is greatest, either because the mass of rubber per unit of volume is least when the volume is greatest, and therefore the quantity of "attracted" carbon bisulphide is least, or because the acetone or acetic ether can penetrate the more easily the greater the distention of the rubber. We are now in a better position to understand the previous statical results which should perhaps have been used to calculate the composition of the *fluid mixture* inside and outside the rubber. For let p be the number of grm.-molecules of acetone per c.c. of fluid mixture inside the colloid, p' the amount outside, and let a and a' have the same values as before. Then $p - ap^2$ will be the pressure of the acetone inside the rubber. This is balanced on the one hand by the volume elasticity of the rubber Kv, and on the other by the acetone outside, whose pressure is $p' - a'p'^2$. Hence.

$$p - ap^2 = p' - a'p'^2 = Kv,$$

or

$$\frac{p + p'}{2} - \frac{ap^2 + a'p'^2}{2} = Kv.$$

If A is the mean between a and a', this expression becomes

$$\frac{p + p'}{2} - \frac{A(p^2 + p'^2)}{2} = Kv,$$

if a and a' do not differ greatly. And if p and p' are not widely different, the last equation will be equivalent to

$$\frac{p + p'}{2} - A\left(\frac{p + p'}{2}\right)^2 = Kv.$$

This equation is the one which has already been arrived at empirically, except that p in the previous equations represented the number of grm.-molecules of acetone per c.c. of expanded rubber instead of per c.c. of fluid mixture in the rubber. The above equation takes no note of

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the initial unequal distribution of the acetone inside and outside the rubber, hence the equation should perhaps be

$$k(p - ap^2) = k'(p' - a'p'^2) = Kv.$$

A more rigid examination would be effected by taking into account the carbon bisulphide as well as the dissolved substance. The equation would then be

$$P - AP^2 + p - ap^2 = KV,$$

where V would equal the total change in volume which the original rubber undergoes, P and p being the mean number of grm.-mols. of carbon bisulphide and the dissolved substance respectively. The displacement of carbon bisulphide by the dissolved substance is not very great at first; hence the omission to consider it would not have much effect on the early part of the curve, but later it would be considerable. This may account for a part of the divergence of the calculated from the observed curve. I hope to work out this consideration at a later date.

Analogy between Vulcanised Caoutchouc and other Colloids.

Colloidal Sulphides.—The previous results seem to throw the most light on the so-called colloidal solutions, such as the sulphides of the heavy metals, ultramarine, &c. These may be considered to consist of particles of the insoluble colloid distended by the osmotic pressure of the water, there being an affinity between the colloid and the water just as there is between vulcanised caoutchouc and carbon bisulphide. The existence of such an affinity is likely since the colloidal sulphides are hydrated bodies. The particles are so small and so greatly distended by water that they remain in suspension, but they are sufficiently large and dense to partially reflect light. If now sufficient saline matter be dissolved in the water, its osmotic pressure will cause the colloidal particles to contract, just as acetone eventually causes rubber distended with carbon bisulphide to decrease in volume. The particles would then be much smaller and denser, and would sink and rapidly agglomerate together. If this explanation is correct a very small quantity of saline matter ought to distend the colloid particles to a greater extent than at first, and should reduce their opacity and rate of subsidence. Whether this is so or not I cannot say. I hope to make experiments on this point. In a similar way to the above the precipitation of soap by common salt may be explained.

Colloidal solutions, such as dialysed silica, alumina, &c., appear to be abnormal, since they cannot be produced by the action of water on the dry substance. There is no form of silica, for instance, which will swell up and go into solution when placed in water. These solutions are, therefore, unstable, since the volume elasticity of the colloids is not balanced by the osmotic pressure of the water and the colloid always separates sooner or later, the water being squeezed out. For this to happen the water must pass from particle to particle of the colloid. If we suppose that free ions can do this whilst water molecules can not, we can understand the effect of small quantities of salts in accelerating the separation of the silica.

If friable silica be placed in strong soda solution it gelatinises and eventually dissolves. Here there is a strong affinity between the silica and the Na ions, and the osmotic pressure of the latter expands the silica much in the same way as carbon bisulphide expands or dissolves caoutchouc. It is known that silica when it dissolves dissociates only to a very slight extent into ions, hence it is allowable to consider it to be infinitely distended when it dissolves in soda. In this case the chemical affinity is used up in doing work in expanding the colloid, and very little heat is produced.

Gelatin, Wool, and Cellulose.—The relation between vulcanised caoutchouc and substances soluble and insoluble in it which have been examined, will probably be found to hold for gelatin; water taking the part of carbon bisulphide, whilst alcohol, acetone, sugar, &c., and possibly

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salts, will be substances having no affinity for gelatin, and which will produce at first an expansion of the swollen gelatin and afterwards a contraction. Precipitants such as tannic acid, chrome-alum, &c., probably combine with the colloid, producing a larger molecule and consequent increase in the volume elasticity, just as sulphur chloride and sulphur unite together molecules of caoutchouc in the process of vulcanising ("On the Vulcanisation of Indiarubber," C. O. Weber, *Journ. Soc. Chem. Ind.*, 1894, p. 11). It is well known that certain dyes, such as violet of methyl-aniline, pass rapidly into gelatin, wool and silk, when these are swollen with water; hence there must be an affinity between these substances and the dye, and it may be possible to determine the molecular weights of such dyes by the extension of a silk thread when placed in their solutions. Such a result would tend to confirm the view that dyeing is a case of solid solution, at any rate in its more elementary aspect. It is also possible by means of the above results to make clear an old phenomenon, which I believe has not yet been explained and which is as follows: If a piece of filter-paper be suspended with one end in a solution of a salt, such as ferric chloride, the salt will rise in the paper along with the water, but will stop short at a considerable distance from the highest point reached by the latter. Now since the water drawn up is continually evaporating, each succeeding portion of the cellulose will be swollen to a less extent. Further, if the composition of the fluid mixture inside the rubber be examined in the acetone experiments (pp. 182–183), it will be seen that the proportion of carbon bisulphide increases as the volume of the rubber decreases, so that the internal fluid would consist entirely of carbon bisulphide when the rubber had contracted sufficiently. If now we write water in the place of carbon bisulphide, and ferric chloride in that of acetone, it is evident that the iron salt will soon be squeezed out and left behind, assuming that there is no affinity between the iron salt and the cellulose, which is probably the case.

Metals.—The relations which have been found for the solubility of substances in caoutchouc will, I think, apply with considerable facility to the influence of dissolved substances on the physical properties of metals. There seems to me to be very good reasons for regarding the metals as colloids, amongst which are their malleability, ductility, and elasticity, the slow softening which some of them undergo when heated, the absence of any definitive molecular weight (Dulong and Petit's law refers to the atom), but most of all the nature of metallic solutions. If a piece of tinned copper be placed in molten tin at a definite temperature, some of the copper dissolves in the tin and the latter probably dissolves to a certain extent in the solid copper. If the temperature be raised, greater quantities dissolve and finally the two metals mix completely, forming a homogeneous liquid. If now the mixture be cooled, the copper does not crystallise out but the two substances generally set as a whole. This behaviour distinguishes the alloy from all solutions of crystalline substances, but not from solutions of colloids such as gelatin. For if the latter be placed in water it swells to a certain extent. If the temperature be raised more water passes into the colloid, and finally when the colloid is "melted" it mixes in all proportions with the water. Now if the solution be cooled, no separation of the gelatin and water takes place but the mass sets as a whole; so that we have here a complete analogy if we consider the copper as being sometimes a colloid. It may be noted that the most malleable metals are those which crystallise in cubes. With three equal axes, the confused arrangement representing a colloid would probably be most easily produced. Now if we return to the rubber expanded with carbon bisulphide, it may be assumed that its tenacity will be less the greater the extension. Now let the carbon bisulphide be gradually replaced by other substances. The effect at first will be the same for all, the substance will exist in the rubber in a "gaseous"* state, and the expansion

* The term 'gaseous' has been used here and in other places for want of a better one, to indicate that state of matter in which the molecules exert no influence on one another.

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will be proportional only to the number of molecules per unit volume; but if further quantities be added the result is very different. If the substance has no affinity for rubber as in the case of acetone, the negative pressure "ap^2" will rapidly neutralise its osmotic pressure and the rubber will soon contract, the maximum volume in the case of acetone being only 104. If, on the other hand, the substance has an affinity for rubber, as in the case of benzene, the negative pressure will be $(a - A)p^2$, that is, it will be small, the substance will remain "gaseous" a much longer time and a proportionately larger volume will be reached, viz., about 107, although benzene "*per se*" can only produce a volume of 91. Now those substances which are most injurious to iron, viz., sulphur and phosphorus, are those which can mix with it in all proportions, and which therefore have a large affinity for iron and would be able to produce a large distension. Moreover, we see that the effect of any one element will be influenced by those already there. Thus, if we gradually replace carbon bisulphide by benzene, the maximum volume attained is greater than that produced by either substance alone; in the same way it is known that the effect of aluminium, silicon, and other elements in modifying the properties of iron depends on the presence of carbon. We may suppose, then, that when these elements are added to iron charged with carbon they at first all produce a slight expansion, which is unimportant, until the maximum volume is reached, and then the volume of the iron begins to decrease and its tenacity and elastic strength to increase. On the other hand, sulphur and phosphorus as already explained produce a considerable expansion before the maximum volume is reached. The distended metal is then near its elastic limit and is consequently very sensitive to shock.

Of course, when we are adding one element we shall be taking away another, but not in equal amount so far as the total mass of iron is concerned. Thus, referring to the original carbon bisulphide and acetone experiments, and considering the constituents inside the rubber only, we have the following results:—

	Inside.		
Vol.	Grm.-mols. CS_2 per c.c.	Grm.-mols. acetone per c.c.	Vol. of added constituents (expansion).
100·00	·01424	0·	86·70
102·58	1376	·00046	89·28
103·76	1330	89	90·46
104·14	1229	178	90·84
100·57	1122	259	87·27
86·93	977	344	73·63
71·52	861	396	58·22
58·76	799	394	45·46
32·77	538	339	19·47
13·3	0·	0·	0·

So that for each state of equilibrium as the volume is decreased we must gradually displace the carbon bisulphide by acetone. Now it is well known that the effect of aluminium and silicon is to displace carbon, which separates in the form of graphite, and such graphite must be considered to be external to the system. To produce a volume of 107 would be impossible with a mixture of carbon bisulphide and acetone, but it could be effected with one of carbon bisulphide and benzene. For benzene we must read phosphorus or phosphide of iron in our "iron" analogy.

In the rubber experiments the constituents inside the colloid are balanced by those outside. This is probably also the case when the metal is submerged in the impurity-giving slag. On cooling some of the constituents may crystallise out. These would be considered to be external to the metal. That such a balance between fluid mixture inside and fluid mixture outside the metal really exists, at any rate when the metal is red hot, is proved by the experiment of M. Lencauchez (Roberts-Austen's "Introduction to Metallurgy," p. 74), in which iron was maintained

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at a red heat for 100 hours in order to allow fluid constituents to diffuse out. At the end of the experiment the metal was found to be coated with grains of slag which had sweated out, the following being the composition inside and outside the metal :—

	Iron.	Slag.
Phosphorus	1·9 per cent.	4–6 per cent.
Silicon	2·6 „	0·6–0·8 „
Graphite	} 3·5 „	0–1·5 „
Combined Carbon	}	0–1·24 „

If the exuding fluid were continually scraped off a simple method of removing phosphorus would be the result, but it would be a very slow one.

Another fact bearing on the idea of a constituent, so dilute as to be "gaseous," acting in opposition to the volume elasticity of iron, is the statement of Roberts-Austen that the tensile strength of electrolytic iron containing 250 times its volume of hydrogen is only 2·7 tons per square inch, whilst after annealing it rises to 15·5.

There are necessarily many considerations which will modify the final result, but it seems to me that it is only by some such theory as the above that it is possible to account for the extraordinary effect which is in some cases produced by small quantities of substances dissolved in iron.

I ought to have pointed out that the boiling-points of phosphorus and sulphur being low as compared with those of other elements found in iron, "a" will be small and $(a - A)$ will be still less. These elements should therefore be highly "gaseous" when dissolved in iron.

Another property of metals of wider application is the change in tenacity produced by the addition of very small quantities of other elements, and which depends only upon the atomic volume of the added element. The following are the atomic volumes of iron and the elements with which it is usually alloyed :—

Carbon	3·6	Chromium	7·7
Boron	4·1	Tungsten	9·6
Nickel	6·7	Silicon	11·2
Manganese	6·9	Arsenic	13·2
Copper	7·1	Phosphorus	13·5
Iron	7·2	Sulphur	15·7

If the added element has an atomic volume greater than that of iron, the tenacity of the latter is increased, and it assumes the hard dense "α" modification. On the other hand, if the dissolved element has an atomic volume less than that of iron, the tenacity is decreased and the iron is found to be in the soft less dense "β" condition. This change of tenacity is not confined to iron but has been shown by Roberts-Austen to apply equally well to gold and other metals, and it is brought about by very small proportions, so that it cannot depend upon the mutual attractions of the "foreign" atoms for one another, but is determined solely by the volume of the atoms relative to those of the metal in question.

I think the effect can be based upon the volume elasticity of the metal, bearing in mind the fact which was pointed out by Prof. Fitzgerald in the last Helmholtz lecture, that although in dilute solutions the dissolved molecules have an osmotic pressure comparable with those of gasses, yet they do not share the easy compressibility of the latter, and can only suffer change of volume under very great pressure.

For this purpose, suppose that a single atom of iron in a mass of the metal be replaced by one of copper. The new atom will exactly fill the space occupied by the displaced one, and will exert an equal pressure. Hence there will be no change in the equilibrium of the parts of the metal, and the mutual attraction of the iron atoms will be balanced by their impacts one on the other exactly as before. If, on the other hand, an atom of iron be replaced by one having a greater atomic volume, the atoms of the iron will be thrust asunder to make room for it since the dissolved atom is practically incompressible. Hence the atoms of the metal inside

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the mass, including the new atom, will be subjected to a pressure by the volume elasticity of the metal. The latter will then be in the compressed or dense "α" modification. Lastly, if the added atom have a less volume than the displaced iron atom, it will exert a less pressure than did the iron atom, the surrounding atoms will close in on it, and the iron will be strained in virtue of its volume elasticity in the opposite direction, so that the metal will be in a stretched condition and will form the less dense "β" modification.

Since colloids may be looked upon as liquids which have failed to crystallise, and may be considered to have many of the properties of liquids, the above considerations may perhaps be applied generally to liquids and concentrated solutions. If this is done, we are able to explain the slight expansions and contractions which take place when organic liquids are mixed. Such changes of volume would not produce any very marked change in properties in the case of liquids, but might very well account for the differences between α and β iron, as already explained. Expansions never take place in making dilute solutions of electrolytes, but always contractions. The strain to which the liquid molecules are submitted might perhaps account for electrolytic dissociation.

Another property of metals which may be explained by the application of van der Waals' equation to dissolved substances is liquation. When a mixture of metals is cooled, a partial separation takes place after solidification, and the constituent of lowest melting-point is always found to have travelled inwards towards the centre. The same is found to be the case with the non-metallic impurities in iron. Now I have considered the outward pressure of a dissolved substance to be $p - ap^2$, or more fully $p - (a - A)p^2$, where ap^2 is the inward pressure due to the attraction of the atoms of the dissolved substance for one another, and Ap^2 the outward pressure due to the attraction between the substance and its solvent—"a" being always greater than "A." Now, as the temperature falls the outward "gas"-pressure "p" decreases and the whole expression becomes negative, the result being that the still fluid constituents will be drawn inwards. As the force "A" is due to the mass of the solvent, its effect will be to direct the condensing substance towards the centre of gravity of the mass.

If the metal be cooled with extreme slowness, liquation takes place to a much less extent, which may perhaps be explained by supposing that the solvent mass crystallises. Diffusion through its mass might then be impossible, since there is no tendency for crystalline solids to diffuse into one another, nor for a liquid to diffuse through a crystalline solid. Solids, on the other hand, will diffuse into colloids. Thus, Sir Frederick Abel has shown that a highly-carburised iron plate will lose carbon to a non-carburetted one even at the ordinary temperature if they are tightly pressed to gether. Again, solid sulphur will diffuse easily into caoutchouc. The above explanation of liquation would perhaps apply to the separation of flints in chalk, especially as the alkalies in the soil would render the siliceous *débris* somewhat soluble. As the molecular weight (or volume) of gelatinous silica is very great, the separation would be very slow.

In connection with the diffusion of colloids into colloids, it would be interesting to see if colloidal sulphur will vulcanise caoutchouc more rapidly than the crystalline element.

Analogy between the Action of Dissolved Substances on Swollen Colloids and on Freezing Liquids

It is usually considered that a liquid in the act of freezing is not homogenous. In some parts of it the molecules are brought together sufficiently closely that they are in the act of forming crystals; in other parts this is not the case. If the molecules forming the "nascent" crystals be considered to represent the colloid in the above experiments, and the other portion of the freezing liquid to represent the fluid surrounding and penetrating the colloid, the first effect of the addition of dissolved

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substances to the freezing liquid will be to drive asunder the crystal-formed molecules, just as dissolved substances at first expand rubber; and from the above experiments the amount of separation will at first be equal for equal numbers of molecules of dissolved salt. The temperature must then be lowered, in order that the crystals may again begin to form; and since the separation of the crystal molecules is equal for equal numbers of molecules of dissolved salt, the lowering of temperature required will also be equal. This analogy between a colloid and the confused agglomeration of molecules representing a "nascent" crystal is rendered more reasonable if we consider a colloid to be intermediate between a liquid and a crystalline solid. The crystallisation of a colloid may either never take place or it may be postponed. The latter condition may apply to metals, and the imperfect separation of copper on cooling a solution of the metal in tin may be due to a tendency of the metal to crystallise: if it were a true colloid, the metallic mixture should always solidify as a whole. The crystallisation of steel under continued concussion would point to the same conclusion, viz., that the crystallisation has been postponed. Colloids, as we have seen, allow substances both solid and liquid to diffuse through their mass, and thus resemble liquids. Crystalline solids, on the other hand, do not allow of any diffusion through their mass. This is probably due to the short range of the forces which bind together the molecules of a crystal. If, for instance, ice be brought into contact with salt, there is probably an affinity between the two substances, just as there is between caoutchouc and carbon bisulphide; but in one case the molecules are torn asunder and separated from one another, the result being that there is a change of state and consequent great absorption of heat: in the other case the solid is simply submitted to a strain, and little or no heat is produced. That this is the case was proved by placing a piece of rubber tubing lightly over the bulb of a thermometer and immersing it in carbon bisulphide. No change of temperature took place. The fact that the heat of "solution" of colloids is practically nought is in favour of the view which has been put forward, viz., that colloids do not readily dissolve, *i.e.*, separate into chemical molecules, but that the volume elasticity of the solid is simply infinitely strained.

Effect of Heat on Colloids.—Indiarubber is peculiar in its relation to heat, in that if it be stretched along one dimension and then be heated it contracts along that dimension and probably expands along the other two, so that the volume expansion is still a positive quantity. This, I think, can be explained on the assumption that there is some diffusing substance in the rubber whose osmotic pressure in all directions would be increased by the action of heat. Now, in the stretched rubber the material is expanded along the longer axis and is compressed along the shorter axes. If the osmotic pressure be now increased in every part, it will assist the volume elasticity of the rubber in those parts which are compressed, but will oppose it in those parts which are expanded; hence the displacement will be greater in the first case than in the second, and the rubber will expand along its shorter axes and will contract along the longer one. This action might be imitated by placing rubber in carbon bisulphide until it has completely expanded, stretching it, and then adding a small quantity of acetone or other substance to the fluid surrounding the rubber: a contraction ought to take place along the longer axis. I hope to carry out this experiment. The result, should it be of the nature expected, should have some bearing on muscle-action, since it would refer muscular contraction to a suddenly produced osmotic pressure.

The diffusing substance in rubber, to which it owes its contraction by heat when stretched, is probably some portion of it more fluid than the rest. The existence of such would be in accordance with the view that it is intermediate between a liquid and a solid, and as a matter of fact it is known that unvulcanised rubber contains two substances of different solubility in carbon bisulphide. The softening of rubber by heat also bears out its intermediate character. Again Mallock has shown that when rubber is greatly stretched it behaves like putty or wet sand, or any other

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mixture of a solid and a liquid ("Physical Properties of Vulcanised Indiarubber," A. Mallock, *Proc. Roy. Soc.*, 1889, p. 233). Such a mixture stretches easily at first, but the expansion abruptly terminates when the fluid portion has been drawn into the interior. Mallock has shown that the same abrupt termination to stretching takes place with rubber.

It may be pointed out in passing that the unequal expansion by heat of crystals may be imitated by means of stretched rubber, the inequality probably depending in each case upon the nature and extent of the strain along the three axes. The previous results on the rate of diffusion of organic liquids into rubber show that this rate is inversely as the molecular volume, which would support the view that rubber has a sieve- or network-structure. Such a structure is also considered to represent the arrangement of the molecules in a crystal. It would be difficult to say what is the exact analogy between the two kinds of substances. If we divide correlated matter into liquids, colloids, and crystalline solids, we can say that in the first a strain is impossible, in the second it can be produced by external forces, whilst it exists in the third in virtue of the polar forces.

In the above work there are many points which require further investigation, but I am obliged to postpone this task, as even in its present state the research has involved a very large amount of work, including some 1,200 weighings and much tedious calculation.

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